GENERAL CHEMISTRY

H. I. SCHLESINGER

SOLUBILITIES OF BASES AND SALTS IN WATER AT 18°.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.0_316 0.0_410	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	0.0_41 0.0_66	0.04 0.0_215	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.0_635 0.0_71	0.006 0.0_317	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 0.0_22
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3	0.16 0.0_292	0.012 0.001	0.0016 0.0_32	0.0076 0.0_214	0.005 0.0_35	0.07 0.003
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.0_314	0.059 0.0_216	0.05 0.001	0.25 0.0_257	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.0_43
OH	142.9 18	116.4 21	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 0.0_32	0.0_35 0.0_45	0.01 0.0_34
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.0_323 0.0_410	0.011 0.0_36	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.0_313
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.0_315	0.006 0.0_31	0.0_338 0.0_415	0.12 0.006	0.4 0.03	73.0 4.3	....	0.0_42 0.0_65
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 0.0_32	1.48 0.030	0.0086 0.0_338	0.0046 0.0_326	0.0_356 0.0_443	0.03 0.0027	0.0_36 0.0_44	0.0_315 0.0_55
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.0_31	4.95 0.10	0.0023 0.0_311	0.0011 0.0_47	0.0013 0.0_313	~0.1 0.01	0.004? 0.0_33?	0.0_31 0.0_43

The *upper number* in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The *lower number* is the molar solubility, *i.e.*, the number of moles contained in 1 liter of the saturated solution.

(Taken from Smith's College Chemistry, through the courtesy of the editor, Professor James Kendall, and the Century Co.)

GENERAL CHEMISTRY

BY

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LONGMANS, GREEN AND CO.
55 FIFTH AVENUE, NEW YORK
39 PATERNOSTER ROW, LONDON
TORONTO, BOMBAY, CALCUTTA, MADRAS
1925

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PREFACE

Long experience in teaching chemistry to students who have had a year of the subject in high school has convinced the author that they should not be given class work or texts planned for those who have had no chemistry at all. Where the two groups are separated, the use of the same text for both causes a sense of dissatisfaction among the better, and lack of application on the part of the poorer advanced students. Moreover, no contribution is made to intellectual growth, in fact superficiality is promoted, if the types of processes, the applications and the historical development of the subject, presented in high school, are described again in college, perhaps with more detail, but with no broader background of the essential facts of organic and physical chemistry than the average freshman possesses.

Consequently, college chemistry for students already somewhat familiar with the rudiments of the science should concentrate on the fundamental phenomena and principles, and on the simpler applications which can be discussed with some degree of thoroughness. The more complex technical processes are thus left to later courses when the student is prepared to take them up from a detailed, scientific point of view. In this way the respect with which chemistry is regarded will be increased far more than by surfeiting the student with descriptions, the scientific significance of which he is unable to appreciate.

Throughout the book, chemistry has been presented as a growing science in which there are many unsettled questions. In the development of the subject from this point of view, no hesitation has been felt about the incorporation of some of the more recent speculations concerning the nature of atoms and molecules, although these newer ideas are admittedly tentative. Here, a new term has been introduced into the discussion of the

valence of elements in compound ions and similar substances. "Valence number" is similar to "polar number" as used by Lewis, but it has been preferred to the latter because it leaves open the question of the nature of the bond.

It has been found convenient, at the University of Chicago, to open the course with two weeks of daily lectures and no laboratory work. In addition to the regular class work, two or three hours per quarter are devoted to voluntary meetings of students whose preparation is deficient in some phase of the subject, such as problem working, equations, etc. In this way unavoidable irregularities in previous training are easily overcome, and the whole class is not penalized for the deficiencies of a small number. The class room work is, of course, supplemented by laboratory instruction, and it is hoped to have ready, before long, a laboratory manual arranged in the order of presentation followed in this text.

The author takes great pleasure in acknowledging the assistance given him by colleagues and friends. Professor J. Stieglitz has given freely of his advice in matters of general policy. Professors W. D. Harkins, G. L. Wendt, R. A. Baker, B. H. Nicolet, and W. A. Noyes, Jr., and Dr. T. F. Young have read the manuscript in whole or in part, and it has benefited greatly by their criticisms. Mr. J. K. Morse was of great assistance in preparing the section on crystal structure. Particular thanks are due Dr. Adeline DeSale Link and Dr. James K. Senior, who have gone over the whole manuscript in detail both from the point of view of contents and of style. The author wishes also to acknowledge the courtesy of Professor Harkins in putting at his disposal an original drawing of the Harkins periodic table, and of Professor James Kendall and the Century Company in permitting him to use certain figures taken from Smith's College Chemistry. Mr. P. Y. Jackson's reading of the proof has been very helpful.

H. I. Schlesinger

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GENERAL CHEMISTRY

CHAPTER I

INTRODUCTION AND REVIEW OF SOME FUNDAMENTAL CONCEPTS AND DEFINITIONS

Chemistry, like any other science, may be studied from two points of view. Interest may be centered on a description of the phenomena and of the body of facts which constitute the science, on its practical applications to daily life and to industry, and on its relations to the various human activities in which it is of importance. This descriptive side of science is the original one, and is the phase which is emphasized in the more elementary presentation of the subject. But as the number of facts increases, they must be unified in some fashion. As a result of this necessity the scientist seeks for guiding principles or theories to relate the myriad details of the growing science to each other and thus to make it easier to bear them in mind.

There is, however, another and far more important factor which leads men to develop theories. The intelligent man is never satisfied with the knowledge of things as they seem to be—he must speculate about the why and the wherefore of all the phenomena which he encounters in life. Also he has learned by experience that, if he wishes to make reasonably rapid progress in broadening his knowledge and in developing the treasures of the earth for his use, he must not allow his search to be haphazard, but must carry it out along some well-considered plan. Many of the theories of science are little more than such a plan, devised for the purpose of systematizing research. A productive theory may be the most practical development of a science because it may greatly shorten the way to the discovery of facts that will be of immediate benefit to mankind.

In the study of chemistry it is of importance to become acquainted, as soon as possible, with its principles and theories. To a certain extent this has been accomplished in more elementary, descriptive courses. Here, however, the main purpose is to present this groundwork of theory and to develop ability to make use of it; descriptions of phenomena and of specific processes are incidental to the main purpose.

Review of Some Fundamental Concepts of Chemistry

Varieties of Matter and Properties.—Everyday experience shows that matter exists in many different varieties. Our senses enable us to distinguish readily between iron and glass, pottery or wood. These differences may be observed irrespective of the quantity in which the particular materials are encountered or of the shapes into which they are cast. Those qualities and modes of behavior by means of which different varieties of matter may be recognized are called "properties." Since matter is known only by virtue of its properties, it is self-evident that two specimens of matter with the same properties are necessarily considered to be made of the same kind of matter; likewise it follows that a given variety of matter must, under the same set of conditions, always have the same properties. It must not be thought, however, that these simple views were always held. The ancient Egyptians and Greeks, for example, spoke of several kinds of gold differing in color and other properties. This was due to their lack, not only of definite concepts about varieties of matter, but also of exact experimental methods for determining whether their gold contained other kinds of matter.

In order to be certain that two specimens are of the same kind or are different, it is often necessary to study the properties with great care. For example, a superficial study of a specimen of sodium chloride and one of potassium chloride does not disclose any differences. Both are white, both consist of crystals having the form of little cubes, the taste is quite similar, each is soluble in water, neither has an odor. But if the properties are examined accurately, that is if they are measured, they are found not to be identical—for example the densities, the weights which dis-

solve in a given amount of water at a fixed temperature, and the melting points are different. Generally, in describing varieties of matter, the chemist does not rely very much on properties like taste and odor, because they are difficult to define; he makes use chiefly of properties such as density, solubility in various solvents, crystalline form, melting and boiling points, because these can be measured with the balance, the microscope, thermometers or other instruments of precision.

Mixtures and Substances.—Examination of various kinds of matter with which the chemist deals discloses the fact that two groups are easily distinguished. The one most frequently encountered in natural products is characterized by the fact that different portions of the same specimen possess different properties. A piece of granite, in which black and white and sometimes red and green specks may be seen, is the usual illustration. Such a specimen must consist of more than one kind of matter. It is a **mixture.** The other group consists of materials all portions of which are absolutely identical—such specimens of matter are called **substances.** The type of mixture which was used above as an illustration, namely granite, is easily recognized as such, but there are mixtures which cannot so readily be classified. For example, a solution of sugar in water is a certain kind of mixture but there are no discontinuities in its properties.

Methods of Distinguishing between Mixtures and Substances.—It is not a simple matter to set down criteria by means of which one can infallibly judge whether a given material is a mixture or a substance. In fact the history of chemistry discloses many an error in decisions of this problem—a particularly interesting one is discussed in Chapter X, page 163. Often painstaking researches must be carried out before the question can be decided. There are, however, two criteria which are very useful in the simpler cases. In the first place, **the relative amounts of the components of a mixture usually vary somewhat,** depending upon the method of preparing the mixture or upon the location in which it is found if it is a natural product. **The most important characteristic of substances is the constancy of their composition.** The second criterion concerns the properties of the material. **In a mixture, the properties are the sum of the properties of the**

components; the properties of a substance are independent of the properties of the materials which have been used in making it.

The difference between mixture and compound formation is illustrated by the following example. Powdered iron and sulfur may be so intimately mixed with each other that the individual particles of each cannot be distinguished with the naked eye. The properties of this mixture, however, are the properties of iron plus those of sulfur, and depend somewhat on the amount of each used. Thus the color may be varied from pure gray to almost pure yellow by using less and less of the iron, the density may be varied continuously from that of iron to that of sulfur, and so on. Sulfur is soluble in carbon disulfide, iron is not; from the mixture this liquid will dissolve the sulfur and leave the iron behind. But if the mixture is heated, it soon begins to glow brightly where the temperature is highest, and the glow travels through the whole mass even though the source of heat is withdrawn; the grayish powder forms a hard, black lump at the bottom of the vessel. Examination of the resulting product discloses none of the characteristic properties of iron or of sulfur. Nothing dissolves in carbon disulfide, provided, of course, all of the sulfur has been used up; the yellow shade has disappeared. The properties of this product are not dependent upon the amounts of iron and sulfur employed, if care is taken to remove all of the unchanged material. In other words, when a new substance is formed as a result of bringing together several substances, the change in properties is abrupt and complete; when nothing but mixing occurs, the change in properties is gradual, because it is merely the adding together of the properties of the components employed.

Although these criteria are sufficient in most cases for the purpose for which they have been described, there are certain instances in which they do not lead to clear cut results. For example, chlorine [1] dissolves in bromine to form a mixture which was, for a long time, thought to contain a compound of the two substances. Since the two are very much alike in behavior, and since the compound was believed to be quite similar to its

[1] See Chapter XI and page 381.

two components, no sharp change in properties was expected to occur when the two were mixed. Only a careful study of the freezing and boiling points of the mixtures finally proved that no compound is formed. On the other hand, the same method of investigation disclosed the fact that bromine and iodine, and chlorine and iodine do form compounds of properties very similar to those of the original components of the mixture.

In such cases decision between mixture formation and formation of a new substance may be very difficult. There are certain kinds of mixtures which under definite conditions have a fixed composition—thus difficulties might again present themselves. Here also the simple methods described do not lead to satisfactory results. Different methods are required for different cases; enough has been said to call the student's attention to the possibility of drawing incorrect conclusions from incomplete data.

Elements and Compounds.—Substances may be broadly classed into two groups, elements and compounds. **Compounds** are substances which can be decomposed so as to yield two or more different substances, or which can be prepared by the chemical union of two or more substances in such a way that the weight of the resulting compound is equal to the sum of the weights of the substances by the union of which they are made.

It used to be customary to define **elements** as substances which cannot be decomposed. The developments of the last ten years have shown, however, that this definition is in need of modification. A considerable number of elements have been discovered to undergo spontaneous decomposition into other elements. This decomposition is in general accompanied by the ejection, from the mass of the decomposing element, of electrically charged material and by a form of radiant energy similar to light but much more penetrating. The phenomenon has on this account been called radioactivity, and these elements, of which radium is an illustration, are called radioactive.

The decomposition of the radioactive elements is not only spontaneous, but no means have thus far been discovered for retarding or hastening the process. On the other hand, many attempts have been made to induce similar decomposition of elements which are stable under ordinary conditions. Thus far

only methods which involve the use of a radioactive element in the decomposition of the stable element have been definitely successful; methods in which use is made of electrical discharges involving extraordinarily large amounts of energy acting through a brief span of time, or of temperatures far above those hitherto attained in any ordinary chemical processes, have given some promise of success.

Because it has thus far been found impossible to control the decomposition of the radioactive elements, and because such extraordinary means have had to be employed to effect decomposition of the stable elements, it has been suggested that an element be defined as a substance which cannot be decomposed into two or more substances by the ordinary chemical means. It is evident, however, that means which today seem extraordinary may, even in the near future, be very commonplace and that this definition is on that account not at all precise. It does nevertheless describe the state of our present knowledge fairly adequately, and the attempt to define the term, element, more satisfactorily will be postponed until, in Chapter XXXIV, the nature of the decompositions which elements undergo has been discussed.

Chemical and Physical Properties and Changes.—The properties by means of which different substances are identified are of two kinds. The **physical properties** of a substance can be described without reference to any other substance; the **chemical properties** always involve one or more substances beside the one under discussion. In the same way physical changes are independent of the presence or absence of other substances; chemical changes involve the presence of more than one substance either in the original material or in that resulting from the chemical change. Physical changes usually do not affect many of the properties of a substance and are temporary in the sense that, when the cause of the change is removed, the properties affected return to their original values. Physical changes in general are gradual. Chemical reactions on the other hand profoundly alter all of the properties of the substance to a greater or smaller extent, the changes produced are not so generally reversible as in the case of physical changes, and the transitions of properties are usually abrupt instead of gradual.

When a piece of platinum wire is heated, the density, elasticity, and conductivity of the wire gradually change as the temperature rises; when the wire is again allowed to cool the properties regain their original values. Thus the changes are gradual and reversible, and most important, they are independent of the presence or formation of any substance other than the platinum itself. The change produced by heat in this case is merely a physical change. When ice is heated its properties change slowly and reversibly until the temperature reaches 0° C.; further heating now produces an abrupt change in some of the properties. But the change is nevertheless reversible, it affects a relatively small number of properties, and it is independent of other substances in the sense that no other substances are required to bring it about or are formed during the course of the change. Melting of ice is to be called a physical change. On the other hand, when a piece of wood is heated above the temperature at which it begins to char, the effects are quite different. New substances are formed as shown by a complete change of properties. The change is abrupt—there is no gradual transition from the original properties to the new ones. The change is irreversible—cooling the products resulting from the heating of the wood does not regenerate the wood. The change is a chemical change.

Again the student is warned not to make distinctions which are too hard and fast. Many chemical changes are reversible. Thus when water vapor is heated to very high temperatures it decomposes into hydrogen and oxygen. When the resulting mixture is gradually cooled, the two elements again recombine. A condition may be realized in which water vapor, hydrogen and oxygen are present side by side. The mixture possesses properties which are the sum of the properties of its components. In this case, however, since the properties of the three substances, water, oxygen, and hydrogen, are so very different, there is no difficulty in recognizing that more than one substance is involved and that the change is a chemical one. Had the substances been quite similar in properties, the answer might have been much more difficult to make. Consider the case of the solution of sugar in water. Although it is true that more than one substance is involved, the process has all of the other characteristics of a

physical change: it is readily reversible; there is no real change in properties for the solution possesses properties which are the sum of the properties of sugar and of water; the components may be mixed in varying proportions. Is the product merely a mixture—the result of a physical change—or is a chemical change involved? The case here dealt with is one about which there is much dispute; it has been introduced into this discussion only to illustrate the futility of trying to force natural phenomena into classifications made merely for convenience; when the attempt at classification is carried *too far* it destroys its own purpose for it ceases to be convenient, and befogs the understanding by giving rise to meaningless controversies.

Two Fundamental Laws concerning Chemical Change.—Experiments, carried out with the greatest care, have shown that so far as our present methods enable us to determine, **the sum of the weights of all of the reacting substances and of all of the reaction products remains unchanged during a chemical change.** It is, of course, essential in proving the correctness of this law to carry out the experiment in such a way that every product is weighed. For example, a candle loses weight as it burns. When the experiment is carried out in such a way that the gases which are the products of combustion are weighed with what is left of the candle, the total weight is greater than the weight of the original piece of candle. But it would be just as incorrect to conclude from the second experiment that there had been a gain in total weight of the substances involved, as it would have been to judge from the first that there had been a loss in weight. The most simple correct way to carry out the experiment is to do it in a closed vessel. When this is done, the weight remains unchanged. The explanation of the apparent gain in weight is, of course, that oxygen of the air takes part in the reaction and that neglecting to weigh the air in which the reaction occurs, before and after the process, must lead to incorrect conclusions.

Toward the close of the last century, a German chemist, Landolt, undertook a most extensive and painstaking test of the **law of conservation of mass** which was briefly described in the preceding paragraph. He sealed two solutions, which were to react with each other, into the two lower parts of an

inverted V tube. After the apparatus and its contents had come to a definite temperature they were weighed. The tube was then tilted back and forth in order to mix the two solutions thoroughly. As a result, the desired reaction took place. The apparatus and reaction products were now weighed again. The balance was contained in a case which could be evacuated to avoid errors due to changes in atmospheric conditions, and balance and apparatus were kept in a constant temperature room. The experimenter manipulated apparatus and balance from a distance by mechanical controls to eliminate errors due to body heat and moisture, and to prevent contaminations by the hands. But even this careful work disclosed no changes in weight as a result of chemical reaction.

The law of conservation of mass is based on no preconceived theory, but is merely a concise statement of the facts thus far discovered. There are, in fact, reasons to suppose that some reactions should be accompanied by changes in the total weight of the reacting substances, but that these changes are too small to be determined by any means at present at our disposal. All laws of science should be interpreted in the same sense as has been the law of conservation of mass. They are to be looked upon as concise generalizations based on the present state of our knowledge; to be sure, those statements which are called "laws" are supported by a large amount of carefully considered evidence, but when new evidence of undoubted correctness is presented which cannot be reconciled with a law, the true scientist is always ready to modify or reject the latter. For this reason it is very important that every student of science should have in mind as clearly as possible the nature of the evidence upon which our modern theories are based.

The second law of chemical change which will be reviewed, is the **law of definite proportions** according to which the **relative weights of substances taking part in a given reaction are always the same**—that is, they are independent of the total amounts employed and of the conditions of the reaction. Thus 16 grams of oxygen react with 2.016 grams of hydrogen to give 18.016 grams of water. If instead of using 16 grams of oxygen, 32 grams are used, 4.032 grams of hydrogen will be required for

complete interaction with the oxygen, and 36.032 grams of water will be formed. The type of experiment upon which this law is based can readily be imagined by the student. It may be pointed out that this law is really a necessary consequence of the law of conservation of mass and of the fundamental property of substances—namely their constancy of composition. Since water is always composed of 11.19 per cent of hydrogen and 88.81 per cent of oxygen, and since the weight of water must be the sum of the weights of the oxygen and hydrogen used in its preparation, it follows that the relative weights of these substances are necessarily fixed in this reaction.[1]

The Importance of Properties.—The importance of thorough knowledge of the properties in the recognition and detection of elements and of compounds, and in determining what substances are best adapted to any particular use is self-evident. But in a broader sense the importance of the study of properties is far greater than is brought out by these considerations of immediate practical application. The study, and particularly the interpretation of properties, involves the most fundamental problem of chemistry. If it is understood why substances possess characteristic physical properties, and are capable of undergoing definite chemical reactions or are resistant to other chemical changes, it will be possible, without waste of time or energy, to produce a substance perfectly suited to any purpose or to predict without delay that a particular problem cannot be solved by chemical means. Such a state of affairs is the ideal of all of the sciences, arts, and industries related to chemistry. Chemical science is as yet a long distance from this ideal, but progress is being made, and one of the main purposes of this book is to give the student some insight into the development of this intensely interesting work which is now making the most rapid strides in its history.

[1] Attention is called to the fact that, although the relative weights of substances taking part in a given reaction are independent of external conditions, the reaction which occurs is often determined by the temperature, the pressure, etc. Thus at elevated temperatures the product of interaction of phosphorus and chlorine is phosphorus trichloride, while at lower temperatures the pentachloride may be obtained.

A moment's thought will make clear that the first step in a discussion of these vital problems of chemistry must be a study of the mechanical structure of matter. Although this phase of the question has been developed largely by physicists, and is on this account more thoroughly treated in text books of physics, a brief presentation of our present knowledge and theories is given in the next chapters.

Notes on the Method of Study

Mere reading of a text book, *whether once or a dozen times*, does not constitute study. Thorough study involves some sort of examination of one's self to make sure that the material presented in every portion of the text is thoroughly understood. It has been the experience of most teachers that making an outline of the portion of the text covered in a chapter is one of the most efficient methods of self-examination. Before attempting to make the outline the student should read the whole chapter, or the portion assigned, fairly rapidly, but carefully, in order to have a survey of the whole material before beginning detailed study. A very useful form of outline is one consisting of a series of questions. Each question should require for its answer the restatement of a definite portion of the text. A student who is able to make such a series of questions knows how to study and understands the text. In order to help the student in carrying out this method of study, each of the earlier chapters is followed by a list of questions which are intended to be used by the student as a guide to the success of his work. Only when he can answer the questions, has he studied the text. In later chapters the questions are intended more to stimulate his ability to think for himself than merely for purposes of review. As the student reads he should decide for himself whether the number of questions is sufficient to serve as a guide for study, and whenever it is not ample, he should supplement the questions in the text by questions of his own devising.

QUESTIONS

(1) What does the chemist mean by the term properties? Which of the following are properties in this sense of the word: Weight, density, color, shape, elasticity, odor? Which of the properties included in the preceding list are suitable for exact measurement?

(2) What two criteria may usually be used to distinguish between substances and mixtures? Of the following which are mixtures and which simple substances: Milk, sugar, salt, an egg, writing ink?

(3) What two methods can you suggest for distinguishing between an element and a compound?

(4) In what respects do chemical changes differ from physical changes? To which class do the following belong: melting of iron, burning of coal? Give your reasons for each decision. Why is the dissolving of sugar a doubtful case?

(5) What is the law of conservation of mass as applied to chemical change?

(6) Show how the law of definite proportions may be derived from the law of conservation of mass and the fact of the constancy of composition of substances.

(7) What is meant by the term "natural law" as used in this text?

REFERENCES

At the close of many of the chapters of this text, and now and then in the footnotes, references to other books and to articles in journals will be given. By reading as many of these as possible the student will greatly broaden his grasp of the subject and, above all, will develop the invaluable habit of independent reading and search of its literature. The references will deal sometimes with more detailed discussions of the subject matter of the chapter in question, sometimes with developments not taken up in this text, and sometimes with applications to industry, to daily life, or to other sciences. Details, such as publishers, etc., of the books cited may be found in the alphabetical index of references on page 605.

For this chapter the following are cited:

MILLARD—Physical Chemistry for Colleges, pages 3–5, gives further descriptions of experiments on the law of conservation of mass.

MELLOR—A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. I, pages 74–93, takes up in detail many of the topics discussed briefly in this chapter. A great deal of interesting historical material and many references to original literature are given.

The treatise by Mellor will be referred to so often that hereafter its name will be abbreviated to "Comprehensive Treatise." It is the best work of reference on general and inorganic chemistry in the English language. While it is very detailed and much too long to be read in its entirety, the style is easy and interesting. It is subdivided into a great many short sections, each dealing with some specific topic. This arrangement makes parts of it useful to all classes of readers. The work is unfortunately not completed at the time this text is written, only four of the contemplated eight or ten volumes being published. But judging from the rate at which the first part was written, there is reason to hope that it will soon be entirely finished.

R. A. GREGORY—Discovery. Chapter VII, deals with the use of the terms "law" and "principle" in science. Many examples from all fields of science are taken up in popular style. Although the book does not deal specifically with chemistry, it is referred to here because it should be of interest to students of general chemistry.

CHAPTER II

THE KINETIC MOLECULAR HYPOTHESIS AND THE GAS LAWS

MATTER exists in three physical states, the solid, the liquid and the gaseous. With these are sometimes included the colloidal and the state of solution. The study of the nature of matter is usually begun with a discussion of gases, not because this state is more important than the others, but because the phenomena exhibited by gases are less complex than those observed in matter in the other states. Thus, to cite only two examples, all gases are miscible with one another in all proportions, and the effect of changes of temperatures and of pressure on the volume of gases is very nearly the same for all substances in the gaseous state.

Characteristics of the Gaseous State.—Matter in the gaseous state is characterized by the fact that it uniformly and homogeneously occupies any space made available to it. If a gas is introduced into a closed vessel at any point, it will soon fill the whole vessel. Not only will there be some of the gaseous substance in every portion of the vessel, but in equal portions there will be equal weights of the gas.[1]

The difference which exists in this respect between substances in the gaseous state and substances in other states is brought out best by a familiar illustration. If liquid water is placed in the lower part of a closed flask, evaporation takes place, and before long even that portion of the flask which contains no liquid water will be filled with its vapor, so that there will be water in every part of the vessel. But the weight of water per unit volume below the surface of the liquid is much greater than its

[1] When very high columns of gas are involved, the effect of gravitation produces an increase of density in the lower portions.

weight in the same volume above the surface. All liquids and solids evaporate and fill the space made available to them, although the amount of material evaporated may be so small that it can hardly be detected, and in some cases cannot be detected at all.

It is thus seen that the difference between matter in the gaseous and in the other states lies in the uniformity and homogeneity of the distribution through space, rather than in the mere fact of the distribution. The distribution of a gas occurs whether the vessel in which it is placed was originally empty or contained some other gaseous substance. And further, just as gases occupy any vessel in which they are placed, so their distribution in the vessel remains uniform when the size of the vessel is changed—for example by altering the position of a piston in a cylinder. But although the uniformity of distribution persists no matter how much the vessel is enlarged it does not necessarily persist indefinitely when the volume of the containing vessel is decreased; for, as will be seen later, on compressing a gas into a smaller volume the gaseous substance may separate into two layers one of which is denser than the other.

Diffusibility and Compressibility of Gases.—A gas, placed in any portion of a vessel, soon distributes itself evenly throughout the vessel. This motion of the gas is called *diffusion*. If the vessel already contains some other gaseous substance, the new gas passes through the other and vice versa. This property leads at once to very important conclusions with regard to the nature of gases. It is clearly easier to explain how two gases can pass through one another if it is assumed that neither consists of a single continuous piece of matter, but that each **is made up of a large number of very minute pieces or particles, called molecules, and that between these molecules there is nothing but empty space.** Upon the basis of this explanation, the gases do not really permeate "through one another"; they filter, so to speak, through the empty spaces surrounding the molecules of each gas. On the further assumption that under ordinary conditions the empty space between the molecules is much larger than the space occupied by the molecules, it also can readily be seen why gases can be compressed, for in the process of com-

pression the molecules are simply pushed closer together. The process of compression cannot be continued indefinitely, for ultimately the molecules will be crowded so closely that they may be said to be in touch with each other throughout the vessel.

Attractive Forces between the Molecules. Velocity of Molecules. Kinetic Molecular Theory.—The assumptions just made must be supplemented by others before they give a reasonable picture of the structure of matter in the gaseous state. Perhaps the most characteristic property of matter is that of attracting other matter. Consequently it is necessary to take this property into consideration when constructing a theory of the nature of gases. The molecules must be assumed to be attracted by the earth and by one another, although these attractive forces need not all be of the same nature. If this is true, it is necessary to explain why the molecules of the gas do not fall to the bottom of the containing vessel in a single clump or ball.

The problem is not without analogy. A similar one had to be solved when the present theory of the solar system was evolved. The sun attracts the planets and the planets attract their satellites; yet each of these bodies maintains its place in the wide distribution of planets, satellites and stars. As is well known, the answer to this question is found in the motions of the heavenly bodies. In the same way the difficulties of the molecular theory are overcome by the assumption that the molecules are in motion, and that the velocity of this motion in substances in the gaseous state is sufficiently great to overcome the attractive forces. The fact that the moon has no gaseous atmosphere has likewise been explained by the assumption, borne out by reliable calculations, that the gravitational attraction of so small a body as the moon is not sufficiently great to prevent the escape from its surface of very rapidly moving molecules. Even though the attractive forces which exist between molecules may be much greater than gravitational attraction alone can account for, it is necessary merely to imagine **the molecules to be possessed of a sufficiently great velocity** in order to understand that they could escape from any attractive force no matter how great. Molecules moving with such velocities would behave as if they were perfectly elastic bodies.

The motions of the molecules are actually very rapid. In oxygen gas at 0° C., their velocity is approximately one-quarter of a mile per second and hydrogen molecules move about four times as fast. But even these enormous speeds are not great enough under all conditions to overcome completely the attractive forces, to which, as will be described in the next chapter, many of the most important properties of matter are due. For the present, however, it will be simpler to discuss an ideal gas—a "perfect gas" as the idealized concept has been called—in which attractive forces are supposed to be completely nullified by the velocity of the molecules.

The **kinetic molecular hypothesis,** as the theory just briefly outlined is called, explains very satisfactorily the phenomena of diffusibility and of expansibility of gases. Gases distribute themselves throughout any space in which they are confined because the molecules of which they are composed are in constant motion. Since it is supposed, for the present, that there are no forces acting which might tend to make the molecules collect in any one portion of the vessel, and since it may further be assumed that **all of the molecules of any one variety of substance are alike,** the distribution through the vessel must be uniform and homogeneous. In moving to and fro within the vessel, some of the molecules come into contact with the walls of the vessel and rebound into the interior, where they strike other molecules and are again driven back to the walls. If the walls of the vessel are imagined to be removed suddenly there is nothing to stop the molecules from moving outward into the new available space—in other words, the gas expands.

Gas Pressure.—Since molecules are particles of matter they must have mass, and consequently must exert a force on any object, such as the walls of the containing vessel against which they strike. As can be seen from Fig. 1,[1] the smaller the volume of the gas, the larger the number of molecules per unit volume, and the greater the number of impacts against the walls. Since the total force depends upon the number of impacts, it is easy to see that decrease in volume must be accompanied by an increase in the force exerted against the walls.

[1] See page 18.

It has been shown by mathematical analysis of the factors involved, that the force (f), exerted by the molecules against unit area of wall surface of the containing vessel, may be expressed by the equation:

$$f = \frac{\frac{1}{3}nmu^2}{v}$$

In the equation, n is the number of molecules contained in the volume v, m is the mass of each molecule, and u is the velocity

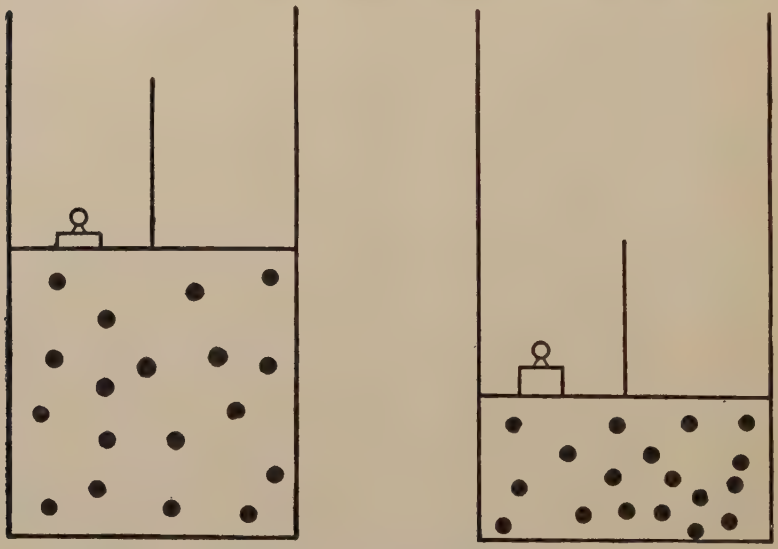


FIG. 1. — A SCHEMATIC DIAGRAM OF A PISTON AND CYLINDER

This figure shows that decrease in volume is accompanied by increase in the number of molecules per unit volume. The larger pressure required to decrease the volume is shown by the larger weight on the piston on the right.

of the molecules. Since a force per unit area is generally called a pressure, p, this equation [1] may be written:

$$p = \frac{\frac{1}{3}nmu^2}{v} \quad \text{or} \quad pv = \tfrac{1}{3}nmu^2 \qquad (1)$$

[1] Students interested in the derivation of these equations will find a simple mathematical discussion in any elementary text book of physical chemistry, such as Millard, Physical Chemistry for Colleges, pages 44–46, Cartledge, Inorganic Physical Chemistry, pages 21–26, etc.

The correctness of these equations may be accurately tested by the behavior of actual gases as is shown below.

Boyle's Law and Charles' Law.—The changes which the volumes of gases undergo when the pressure or the temperature is changed, are described in two well-known laws. The first of these is the law of Boyle and Mariotte, more commonly known as **Boyle's Law,** which states that the volume of a given weight of gas is inversely proportional to the pressure if the temperature be kept constant. It is likewise well known that to increase the weight of gas in a given volume and at a given temperature, the pressure must be increased in direct proportion to the increase in the weight. These statements may be condensed into the simple equation:

$$p \times v = w \times (\text{constant})_t \qquad (2)$$

p and v are the pressure and the volume of the gas respectively, and w is its weight. The expression $(\text{constant})_t$ is used to indicate that to make the right-hand member of the equation equal to the left, w must be multiplied by a certain number which does not vary no matter how much p, v, or w may be changed, provided the temperature, t, remains the same.[1, 2]

[1] The student should assure himself that equation (2) has the same meaning as Boyle's law by working the following problem. 1 liter of oxygen gas at 0° C. and under a pressure of 760 mm. weighs 1.429 grams. Substitute these values for the volume, the pressure, the temperature and the weight in equation (2), and calculate the value of "$(\text{constant})_t$." In order to find the volume of 1.429 grams of oxygen at the same temperature and at 380 mm. pressure, substitute in the equation this value for the pressure and 1.429 for the weight, the value found for the constant, and solve for v. In the same way, the pressure at any volume for the same weight can be found, or the pressure can be calculated if the volume is kept constant and the weight is changed.

[2] Subscripts are frequently used, as in equation (2) to indicate limitations or restrictions placed upon symbols. Thus the subscript in the expression $(\text{constant})_t$ indicates that the value of this term is constant only if the temperature is constant. Should the discussion of equation (2) be limited to cases in which the weight is not changed, the whole of the right-hand member of the equation would have a constant value as might be indicated by writing $p \times v = (\text{constant})_{w,t}$. The two subscripts mean that both the weight and the temperature of the gas must remain the same in order that the equation be correct. A similar use of subscripts is found on page 26 where they are employed to indicate to which of two gases the symbol has reference.

The second law referred to above is that of **Charles and Gay-Lussac,** which summarizes well-established facts with regard to the influence of temperature changes on the volume of gases at constant pressure. It states that for each centigrade degree rise or fall of temperature above or below 0° C., the volume of any gas is increased or decreased by approximately $\frac{1}{273}$ of its volume at 0°. A condensed form of this statement is the equation:

$$v_t = v_0 + \left(\frac{t}{273} \times v_0\right) \tag{3}$$

in which v_t represents the volume at the centigrade temperature t, v_0 the volume at the temperature 0° C. and t the number of degrees centigrade rise or lowering of temperature from 0° C. If the gas has been cooled below 0°, t is a negative quantity; if the gas has been warmed to a temperature above 0°, t is a positive quantity. Thus, if at 0° the volume of a gas is 100 c.c., it will be $100 + (\frac{10}{273} \times 100) = 103.66$ c.c. at $+10°$ C. or $100 - (\frac{10}{273} \times 100) = 96.33$ c.c., at $-10°$ C.

Equation (3) may, by simple algebra, be transformed into the expression:

$$v_t = v_0 \frac{(273 + t)}{273} \tag{4}$$

The law of Charles and Gay-Lussac is applicable to all gases; hence, irrespective of the kind of gaseous substance and the temperature, the term $(273 + t)$ always appears in the equation. It is therefore convenient to replace the sum, $273 + t$, by the letter T and to call it by a special name, the "**absolute temperature.**" Obviously the latter is simply a number larger by 273 than the centigrade temperature. In this connection it is interesting to note that if t, i.e., the centigrade temperature is lowered to $-273°$, v_t according to equation (4) becomes zero. Hence some sort of significance may be attached to this temperature, the "**absolute zero**" as it is called.[1] Aside from its theoretical interest which need not be considered here, the use of the absolute temperature, T, as defined above, simplifies equation (4). For

[1] It has been suggested that at the absolute zero all molecular motion ceases.

if the symbol T is substituted for the term $(273 + t)$, equation (4) becomes:

$$v_t = v_0 \frac{T}{273} \tag{5}$$

Equation (5) can be transformed into a more general form. If the volume of a gas is v_1 at the absolute temperature T_1, and v_2 at the absolute temperature T_2, then:

$$v_1 = v_0 \frac{T_1}{273} \tag{5a}$$

$$v_2 = v_0 \frac{T_2}{273} \tag{5b}$$

Since equation (5) is true at all temperatures, dividing equation (5*a*) by equation (5*b*) gives:

$$\frac{v_1}{v_2} = \frac{T_1}{T_2} \tag{6}$$

In words, instead of in symbols, **the volume of the gas is directly proportional to its absolute temperature** if the pressure remains unchanged.

The facts concerning the effects of changes in pressure, in temperature, and in the weight, upon the volume of gases can be expressed in the form of a single equation:

$$p \times v = w \times T \times (\text{constant}) \tag{7}$$

The symbols p, v, w and T have the significance already assigned to them. The term (constant) is used to indicate that the left side of the equation is equal to the right only if the product $w \times T$ is multiplied by a number which is the same for any volume, pressure, weight or absolute temperature but which varies for different substances.[1]

Actual Behavior of Gases and Kinetic Theory.—This discussion of the actual behavior of gases makes it possible to com-

[1] The student should make sure that equation (7) describes exactly the behavior of gases by means of the method given in footnote 1, on page 19. In other words, he should prove by means of a problem which he can set for himself, that equation (7) shows the volume to be directly proportional to the absolute temperature and inversely proportional to the pressure, etc.

pare the experimental facts with equation (1), developed entirely on theoretical grounds from the kinetic molecular theory:

$$p \times v = \tfrac{1}{3}nmu^2 \qquad (1)$$

The left-hand members of equations (1) and (7) are identical. Equation (1) may be written

$$p \times v = \tfrac{1}{3}wu^2, \qquad (1a)$$

since $n \times m$ is the mass of all of the molecules of the gas in volume v, and is therefore equal to w, the total weight of the gas. If it is now assumed that u^2 is proportional to the absolute temperature, equation (1*a*), which is derived entirely from theoretical considerations, becomes identical with equation (7) which is based entirely on experiment.

This agreement leads at once to another conclusion concerning the **kinetic energy of the molecules.** Kinetic energy is defined by the expression, $\frac{1}{2}mu^2$, in which m is the mass and u is the velocity of the body under consideration. Since, for the case of molecules of a given variety of matter, the mass is always the same and since the square of the velocity (according to the kinetic molecular theory) is proportional to the absolute temperature, the **kinetic energy of the molecules must also be proportional to the absolute temperature.** Comparison of the actual behavior of gases with the equations derived from the kinetic molecular hypothesis, has therefore led to the interesting conclusion that the (absolute) temperature of a gas must be a measure of the kinetic energy of the molecules, and also that rise of temperature increases the kinetic energy by increasing the velocity [1] of the molecules and *vice versa.*

[1] The term velocity, as used in connection with the equation $pv = \frac{1}{3}nmu^2$ really means the velocity of a molecule possessing average kinetic energy. At any moment some of the molecules are just striking a wall of the vessel; at this moment they are changing from a motion toward to one away from the wall, and may be considered not to be moving at all. In the same way molecules are striking other molecules, and some lose velocity in a given direction while some acquire increased velocity. But the velocity of a molecule possessing average kinetic energy in any part of the gas at a given temperature is the same as that in any other part at the same temperature.

Practical Applications of the Gas Laws.—Equation (7) makes it possible to calculate the volume of a gas at any temperature and pressure if the volume at any other temperature and pressure be known. At the temperature T, the pressure p, and the volume v, equation (7) reads:

$$p \times v = w \times T \times (\text{constant}) \tag{7}$$

If the new temperature, pressure and volume are respectively T', p' and v', it becomes:

$$p' \times v' = w \times T' \times (\text{constant}) \tag{7a}$$

Dividing equation (7) by (7a) gives:

$$\frac{p}{p'} \times \frac{v}{v'} = \frac{w \times T \times (\text{constant})}{w \times T' \times (\text{constant})}$$

This of course becomes simplified to read:

$$\frac{p}{p'} \times \frac{v}{v'} = \frac{T}{T'}$$

If it is desired to calculate the volume of a gas at any temperature or pressure from the volume at any other temperature and pressure, the last equation may be put into the form:

$$v' = v \times \frac{p}{p'} \times \frac{T'}{T} \tag{8}$$

This equation can be used directly to make the desired calculations. It is necessary, however, to decide what units are to be used for the various quantities involved. From the way in which equation (7) was derived, it follows that the temperature **must** be expressed in terms of the absolute scale, i.e., that $T = 273 + t$, if t is the centigrade temperature. The other terms may be expressed in any desired units provided the same units are used throughout any given calculation. For volume, the most common unit in scientific work is the cubic centimeter or the liter. For pressure, it is customary to use the number of millimeters to which the pressure of the gas could raise a column of mercury (at 0°). Another common unit for the pressure is the "atmosphere." A pressure of one atmosphere is the same as a pressure of 760 millimeters of mercury.

The following problems are illustrations of the use to which equation (8) may be put. Suppose a given weight of gas at 30° C. and at a pressure of 500 mm. occupies a volume of 100 c.c.; the volume which it would occupy at 40° C. and 750 mm. may be calculated. The terms v, p, and T then have the values 100, 500 and (273 + 30) respectively, and p' and T' are 750 and (273 + 40) respectively. Hence

$$v' = 100 \times \frac{500}{750} \times \frac{(273 + 40)}{(273 + 30)}$$

This equation is obtained simply by substituting the values given above for v, p, T, v', p' and T' in equation (8). Since there is a possibility of making an error by confusing the numbers to be used for p or p' and for T or T', the student is not advised to work such problems by an attempt simply to substitute numbers in the equation. He is advised to consider before working each problem what effect the pressure and the temperature changes will have upon the volume. Thus, in the problem just solved, the pressure changes from 500 mm. to 750 mm. This is an increase in pressure and causes a decrease in the volume. The fraction $\frac{p}{p'}$ must therefore have a value smaller than 1 and must be $\frac{500}{750}$. In the same way it is seen that the change in temperature, a rise, must increase the volume. The fraction $\frac{T'}{T}$ must, therefore, be larger than 1 and will be $\frac{(273 + 40)}{(273 + 30)}$. By refraining from mechanical substitution, errors are avoided.[1]

Problems involving equation (8) in an indirect way can be solved in a similar way. The density of air at 0°, 760 mm. is known to be 1.293. What then is the density of air at 25° and 770 mm.? The density is the weight of 1 liter of the gas.[2] Now on changing the temperature from 0° to 25° the gas expands, and some of it must leave the vessel if the pressure is not changed.

[1] Problems 13, 14, and 15 at the close of the chapter are of this type. By working one or two of them at this point, understanding of the discussion is assured.

[2] Sometimes the number of grams per 1 c.c. is used.

The weight of gas remaining in the liter space is less than it was at the lower temperature, and the density is decreased by the fraction $\frac{273}{(273 + 25)}$. On the other hand, by changing the pressure from 760 mm., to 770 mm. the gas is compressed, and more of it must be introduced to keep the volume at 1 liter. The weight of gas in the liter space is greater at the higher than at the lower pressure, and the density must be increased by the fraction $\frac{770}{760}$. The density of air at 25°, 770 mm. will, therefore, be:

$$1.293 \times \frac{273}{(273 + 25)} \times \frac{770}{760}$$ [1]

Standard Conditions.—Although it is very often necessary to calculate the volume of a gas at any specified pressure and temperature, these equations are most commonly used to determine the volume of a given quantity of gas at 0° and 760 mm. In comparing gases with one another, it is self-evident that the comparison should be made for the gases under similar conditions. On the other hand it is not always convenient to carry out the measurements under identical conditions. It has, therefore, been decided to refer the measurements to a standard temperature and pressure, namely 0° and 760 mm., by the type of calculation already illustrated. This calculation is called "**reducing to standard conditions.**" The phrase "standard conditions of temperature and pressure" will occur so often in our work, that the abbreviation **S. C.** will prove convenient.

Dalton's Law of Partial Pressures.—Another fact about gases which is of considerable practical importance can also be shown to be in full agreement with the kinetic molecular theory. Thus far only the case of pure gases has been considered. Just as frequently the chemist deals with mixtures. In a mixture of gases, each gas exerts its pressure as if the other gas were not present. The pressure exerted by each is called the partial pressure of that gas, and what has just been said may be restated as follows: **the total pressure of a mixture of gases is equal to the sum of the partial pressures of the gases constituting the**

[1] Further illustrations of this type of problem are given in Exercises 24, 25 and 26, at the end of the chapter.

mixture. Thus if enough of one gas to produce a pressure of 1 atmosphere is put into a vessel, and another gas is then added to the first in such quantity that it, if alone present, would also have produced a pressure of 1 atmosphere, the pressure actually existing in the vessel when both are present is 2 atmospheres. A simple consideration of the matter in the light of the kinetic theory shows that this result is just what the theory would lead one to expect, provided the molecules of the two gases do not exert appreciable attraction upon one another nor affect one another in any other way. The fact, however, was known before the theory was well established, and contributed to its acceptance. Like the other facts about gases this one has been called a law and named "**Dalton's law of partial pressures,**" after its discoverer. Its usefulness is illustrated by the following example.

Correction of the Volume of a Gas for Water Vapor.—If a gas is collected over water, or passed through water, it will ultimately become saturated with water vapor. Consequently, if the pressure on the gas before and after it has been brought into contact with water is kept the same, the volume will increase because the volume of the water vapor has been added to that of the gas. As a result of the increased volume, the pressure of the gas itself, that is, its partial pressure, will be smaller than the total pressure of the mixture of gas and water vapor. If the total pressure is called p, that of the gas in question p_{gas} and that of the water vapor p_w, the law of partial pressures says that:

$$p = p_{\text{gas}} + p_w. \tag{9}$$

Now the total pressure, p, can be very easily measured. The partial pressure of the water vapor, p_w, depends only on the temperature of the water alone and, as will be seen in a later chapter, is known if this temperature is known. Consequently it is possible to calculate from the simple equation just given what the partial pressure of the gas, p_{gas}, must be. Thus at 25° C. the pressure of water vapor in contact with liquid water is 23.6 mm. If a gas is collected over water at this temperature and the total pressure of the mixture of the gas and water vapor is 750 mm.,

the pressure which would be exerted by the gas, if it alone were present in the same volume, is 726.4 mm. Assume that the volume of the mixture is 100 c.c. Since the pressure of the gas in this mixture is only 726.4 mm. and the temperature 25°, it follows that, in order to find out what the volume of the gas would be if it alone were present without water vapor at 760 mm. and 0°, a correction must be made to standard conditions from the pressure of 726.4 mm. and the temperature 25°.[1]

Rate of Diffusion of Gases.—Another useful example of the way in which the kinetic theory may be applied comes from the equation

$$p = \frac{\frac{1}{3}nmu^2}{v}$$

As has already been pointed out the product $n \times m$ is the weight of the gas contained in the volume v. By definition, the weight of any substance divided by its volume is its density (d). Hence the preceding equation may be written:

$$p = \tfrac{1}{3}du^2$$

Suppose now that two different gases are both at the same temperature and pressure. For the first and for the second gas, the two equations $p = \frac{1}{3}d_1u_1^2$ and $p = \frac{1}{3}d_2u_2^2$ may be written. d_1 is the density of the first gas, and u_1 the velocity of its molecules, while d_2 and u_2 represent the same quantities for the second gas. Dividing the first of these equations by the second gives:

$$\frac{d_1}{d_2} = \frac{u_2^2}{u_1^2}$$

This equation can be cast into the form:

$$\frac{u_1}{u_2} = \sqrt{\frac{d_2}{d_1}}$$

In words, velocities of the molecules of two gases are inversely proportional to the square roots of the densities of the gases.

[1] Additional practice in problems like this may be obtained by working Exercises 16 and 17 at the end of the chapter.

In practice the velocity of molecules of gases is not of much importance. What greatly interests the chemist for the solution of many **practical** problems is the rate of diffusion of gases. Why these two—that is, the velocity of the molecules and the rate of diffusion of a gas—are different quantities will become clear upon consideration of the way in which any given molecule of a gas moves from one point of a vessel to another. Suppose a molecule is starting on an upward path through a vessel containing a gas. Before it has gone very far it may collide with another molecule. As a result of this condition it rebounds downward again. It again collides with another molecule and rebounds upward, but perhaps in an oblique direction. An oxygen molecule, for example, in the gas at 0°, 760 mm., travels on the average only about 0.00003 cm. before it strikes another. For this reason, although the height of the vessel may be only a centimeter, a molecule in traveling from the bottom to the top travels many times that far. Hence, it takes the molecule a relatively long time to traverse the centimeter from the lower to the upper wall of the vessel, even though its velocity is actually very great, because the molecule instead of taking a direct path travels by a very devious one. It is evident that the more molecules there are in the vessel the greater will be the number of impacts and, consequently, the more interruptions to its progress. Hence, the rate of diffusion depends upon the number of molecules, in other words upon the pressure, in spite of the fact that the velocity of the molecules is independent of the pressure. But it can be shown that the rate of diffusion at a given pressure depends on the velocity of the molecules, and from this consideration and from the equation developed above, it follows that the **rates of diffusion of two gases likewise vary inversely as the square roots of their densities.** Thus, since at 0°, 760 mm. the density of hydrogen is approximately 0.09 and that of oxygen 1.429, the rate of diffusion of hydrogen will be to that of oxygen as $\sqrt{1.429}$ is to $\sqrt{0.09}$, or as 3.95 : 1, which means that hydrogen diffuses about 3.95 times faster than oxygen.[1]

[1] Because of a number of complicating factors, this relationship holds only approximately for the rate of diffusion. But it is exact for the rate

In order to review the material contained in this chapter, and to make sure of understanding it, the student should answer the questions and problems given below.

EXERCISES AND PROBLEMS

(1) What are the three states of matter and why is the discussion of the nature of matter usually introduced by a discussion of gases?

(2) (*a*) In what respect do gases differ from liquids and solids? (*b*) How do liquids differ from solids?

(3) (*a*) What is the evidence upon which the idea that gases consist of molecules is based? (*b*) Why is it thought that the "empty" space between molecules of gases at ordinary pressures is large compared to the size of the molecules?

(4) Why is it necessary to assume that the molecules are moving at relatively high velocities at ordinary temperatures?

(5) Explain the mechanism of compression and of expansion of a gas from the point of view of the kinetic molecular hypothesis.

(6) What is the cause of the pressure exerted by gases?

(7) Show by means of a problem of your own devising that equation (2), page 19, is a restatement of Boyle's law.

(8) Show how equation (6) is derived from equation (3) page 20.

(9) Show what assumption must be made in order that equation (1) may become identical with equation (7).

(10) According to the kinetic theory, what does the temperature of a substance measure?

(11) (*a*) What is the partial pressure of a gas? (*b*) What is Dalton's law of partial pressures?

(12) (*a*) Why is the rate of diffusion of gases at ordinary pressures and temperatures slow, although the velocity of the molecules is great? (*b*) How could the rate of diffusion be increased without raising the temperature? Why?

(13) A gas whose volume is 100 c.c. at 20° C. and 700 mm., is heated to 50° C. and the pressure raised to 750 mm. What is its volume under the new conditions? (*Ans.* 102.6 c.c.)

NOTE.—In working problems of this sort the student should avoid waste of time, spent on multiplying and dividing, by using

of effusion, that is the escape of a gas through a small opening, because the complications due to the viscosity of the gas and the dimensions of the molecules are eliminated.

a table of logarithms or a slide rule. Four-place logarithms or slide rules about 25 cm. in length, or even shorter, are fully accurate enough. For one problem of each type the answer is given. This enables the student to make sure that he is using the correct method for solving the problem. But he can gain self-confidence only by working problems whose answers are not given, and learning to rely on his own judgment about the correctness of his work.

(14) If the volume of a gas is 150 c.c. at 25° C. and 750 mm., what is its volume at −10° C. and 700 mm.? (*Ans.* 141.9 c.c.)

(15) If the volume of a gas is 25 c.c. at 30° C. and 740 mm., what is its volume at 50° C. and 600 mm.? What would be its volume at −15° and 750 mm.? At −30° and 850 mm.?

(16) A gas collected over water at 18° C. has a volume of 100 c.c. when the pressure is 740 mm. What would be the volume of the dry gas at 0° C., 760 mm.? (The partial pressure of water vapor over water at 18° is 15.4 mm.) (*Ans.* 89.46 c.c.)

(17) A gas collected over water at 24° has a volume of 230 c.c. when the total pressure is 750 mm. The partial pressure of water vapor over water at 24° is 22.2 mm. What would be the volume of the dry gas at 10°, 730 mm.?

(18) One liter of gaseous hydrogen weighs approximately 0.09 gram at S. C. What weight of hydrogen would be required to fill a rigid balloon whose capacity is 3000 liters if the temperature and pressure within the balloon are to be respectively 20° and 740 mm.?

(19) A gas has a volume of 30 c.c. at 20° C. and 740 mm. At what pressure will the volume be 50 c.c., if the temperature is also changed to 30° C.? (*Ans.* 459 mm.)

(20) A gas has a volume of 45 c.c. at 25° C. and 730 mm. At what pressure will its volume be 20 c.c. if the temperature is changed to 10°?

(21) A gas has a volume of 600 c.c. at 35° and 400 mm. At what temperature will its volume become 450 c.c. if the pressure has been changed to 750 mm.? (*Ans.* 160°. NOTE.—Calculate the absolute temperature and convert the result to centigrade degrees.)

(22) A gas has a volume of 650 c.c. at 15° and 725 mm. At what temperature will its volume be 300 c.c. if the pressure has been changed to 450 mm.?

(23) Suggest a method of proving the correctness of your answer to problem 22. (The same sort of method may be used for problem 20).

(24) At 375 mm. and 45° C., a gas has a density of 2.5. What is its density at 20° C. and 750 mm.? (*Ans.* 5.426.)

(25) One liter of a gas at 27° and 700 mm. weighs 1.7 grams. What would be the weight of 1 liter of the same gas at −10°, 750 mm.?

(26) A gas at 25°, 725 mm. has a density of 2.0. What would be the weight of 1 liter of it at 20°, 760 mm.?

(27) The weight of 1 liter of carbon dioxide at S. C. is 1.977 and that of nitrogen, 1.251 grams. What are the relative values of the rates of diffusion of the two gases?

REFERENCES

Several are given in footnote 1, page 18.

MELLOR—Comprehensive Treatise, Vol. I, Sections 2, 4 and 6, deal with the laws of Boyle, Charles and Dalton.

J. PERRIN—The Atoms (translated by Hammick) pages 48–50, 53–64, and 81–82 are of interest in connection with this chapter of the text.

ALEMBIC CLUB REPRINTS—This is a series of reprints and extracts of papers of historical interest. Several of them will be cited in later chapters.

FOUNDATIONS OF THE MOLECULAR THEORY. (Reprint Number 4) —Papers and Extracts from John Dalton, Gay-Lussac and Avogadro (1802–1808).

CHAPTER III

THE KINETIC MOLECULAR HYPOTHESIS AND THE DEVIATIONS FROM THE GAS LAWS

Preliminary Discussion of the Phenomena of Liquefaction of Gases and of the Crystallization of Liquids

Although the gas laws (that is Boyle's law, the law of Charles and Gay-Lussac and Dalton's law of partial pressures) describe fairly accurately the behavior of gases when the pressures are low and the temperatures are relatively high, this agreement between fact and formula is not found at moderately high pressures or low temperatures. Under the latter conditions the deviations in the behavior of actual gases from the demands of the gas laws may be illustrated by plotting the actually observed value of the product $p \times v$ (pressure times volume) at some constant temperature against the value of p. Thus, in Fig. 2, the values of $p \times v$ are plotted as ordinates and the values of p as abscissae. The scale used is an arbitrary one. Since according to the gas laws, the product $p \times v$ at a given temperature should have the same value no matter what the pressure may be, the plot for this product should be a straight line as has been indicated in the figure by the dotted line. When this is compared with the line which represents the actual value of $p \times v$ for hydrogen, it is at once seen that hydrogen behaves as would be

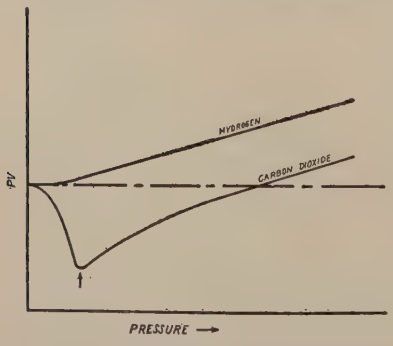


Fig. 2. — Different Types of Deviation from the Gas Laws.

The units are arbitrary and the drawing schematic.

expected from the gas laws when the pressure is low, but that the value of $p \times v$, instead of remaining constant, gradually rises as the pressure is increased, and when the pressure becomes quite large, rises fairly rapidly. In the case of carbon dioxide, the actual behavior of the gas differs even more greatly from the theory than it does in the case of hydrogen; the product, $p \times v$, even at moderately low pressures, falls below the straight line, then curves upward again, and ultimately rises quite rapidly to a value much higher than the original one.

Deviation Due to the Volume of the Molecules.—In the equation $p \times v = w \times T \times$ (constant), it is customary to consider the volume v to include all of the space enclosed by the walls of the vessel in which the gas is confined. That space, however, is partly occupied by molecules; in other words, the space in the vessel consists of "truly empty space + space occupied by molecules." Since only one molecule can occupy a given portion of space at any one time, the value which ought to be used for v in the equation should be the "empty space" because, from the derivation of the gas laws, v is the volume in which the molecules are free to move. The value for v which is customarily used is, therefore, larger than the value which ought to be used, and the product $p \times v$ consequently is larger than it should be. When the pressure is very small and the total volume very large, the space occupied by the molecules is such a small fraction of the total volume that the sum "empty space + space occupied by the molecules" is not appreciably different from the "empty space" alone. But as the gas is compressed, the "empty space" decreases while the "space occupied by the molecules" remains practically unchanged, since the molecules are relatively incompressible. The effect therefore is that the difference between the terms "the empty space" and the "empty space + space occupied by molecules" becomes greater and greater. In this way the deviation from the gas laws, as exhibited by hydrogen, is easily interpreted.

Deviation Due to Attractive Forces.—In the description of the kinetic theory it was pointed out that since gravitational attraction is one of the most fundamental properties of matter, molecules must likewise be supposed to attract one another,

although it is not likely that this attraction is of exactly the same nature as gravitational attraction. The attractive forces were disregarded in the preceding chapter, in which the discussion was limited to gases under moderate pressures. When, however, the molecules are brought closer together by larger pressures, the attractive forces assume greater importance, since all such forces increase as the distance between the bodies decreases. A molecule moving toward the wall of a vessel will strike the wall a harder blow if it is moving freely, than if it is being pulled back from the wall by the attraction exerted by the molecules in the interior of the vessel. The effect of attractive forces is therefore to make the pressure, and hence the product $p \times v$, smaller than it would be if there were no such forces at play.

The curve for carbon dioxide shows that, when the molecules are brought close enough together by increased pressure, the actual product, $p \times v$, is smaller than the one calculated from the gas laws—smaller, that is, than the value calculated without considering the attractive forces. But when the molecules are brought still closer together, the volume influence, discussed in the preceding paragraph, comes into play also, and as its effect is to make the product, $p \times v$, larger, the two influences tend to counteract each other. The product tends therefore to become constant as shown by the flattening of the curve at the point indicated by the arrow. As the increasing pressure crowds the molecules still closer together, the volume influence begins to predominate and the product, $p \times v$, increases again.

Nature of the Attractive Forces.—It should be noticed that the deviation of hydrogen from the gas laws could be satisfactorily explained on the basis of the volume effect alone, whereas to interpret satisfactorily the more complicated behavior of carbon dioxide both volume effect and attractive forces had to be taken into consideration. This cannot be due to an unusually large volume effect for hydrogen, for there is no reason whatever to believe that the space occupied by hydrogen molecules is extraordinarily large. The difference in the two cases must therefore be due to a difference in the strength of the attractive forces; those between the molecules of carbon dioxide must be considerably greater than those between hydrogen molecules.

The existence of such differences points to the conclusion that the attractive forces are not essentially gravitational because gravitation is independent of the nature of the matter attracted. It is also found that the attractive forces between molecules are in general very much greater than gravitational attraction could account for. The nature of these forces is not exactly known.

The deviations in the pressure and volume of gases make it necessary, for work of the highest accuracy, to introduce correction terms into the equations used for reducing the volume of gases from one pressure and temperature to another. The equations by means of which this may be done are too complicated to be discussed here. Wherever it is of sufficient importance, data given in this text have been corrected for these deviations. Such corrected data will, however, always be indicated by the symbol (corr.), to make it clear that they are not the original experimental values. The deviations from the gas laws are also of importance in practical work. Although at ordinary temperatures and pressures the deviations commonly amount to only 1 to 5 per cent, that *percentage* may make a very large difference in the actual volumes when large quantities of gas are involved.

Liquefaction and Solidification.—As the pressure of a gas is increased, the molecules are forced more and more closely together, and the effect of the attraction between them becomes greater and greater. If the temperature is lowered at the same time, the kinetic energy of the molecules, which counteracts the attractive force, becomes smaller. A point must, therefore, ultimately be reached at which the attraction is so great and the kinetic energy so small that the molecules moving at the average velocity are no longer able to escape from one another. The substance has then lost the property of distributing itself uniformly and homogeneously throughout a space of any size—it is no longer a gas. If the process of cooling and compression is stopped when the molecules are still so far apart that the substance is capable of a limited amount of free motion, the gas is transformed into a liquid.

Continued lowering of the temperature now further decreases

the kinetic energy and, therefore, further increases the tendency of the attractive forces to draw the molecules towards each other. A point is finally reached at which it is impossible to pack the molecules more closely together without having them arrange themselves in some definite way. To understand this one can use the analogy of packing a trunk. A carefully packed trunk holds more than one into which the articles have been thrown carelessly. At a sufficiently low temperature, when the molecules are packed together as closely as possible by the attractive forces, they take on definite arrangements which result in the formation of crystals—in other words the substance has now been transformed from a liquid into a solid. Although this description of the structures of solids and liquids is quite incomplete and will be amplified in a later chapter, it makes clear that the kinetic molecular theory applies to matter in all of its states.[1]

Critical Phenomena. Freezing Point.—From the discussion of the factors which cause the transformation of a gas into a liquid, it is apparent that this change will not take place if the kinetic energy is sufficient to overcome the maximum attractive force between the molecules of a gas. Under these conditions it is necessary not only to increase the pressure but also to lower the temperature of the gas, since the lowering of the temperature decreases the kinetic energy. There must be a temperature above which a gas cannot be liquefied, no matter how much the pressure is increased. The highest temperature at which it is possible to liquefy a gaseous substance by applying pressure is called the **critical temperature** of that substance, and the pressure which must be applied at this temperature to produce liquefaction is called the **critical pressure.** The critical temperature and critical pressure are characteristic properties

[1] The explanation that solidification is due to forcing the molecules into close packed arrangements, does not account for the expansion of water on freezing. Water is one of a few exceptions because, in most cases, freezing is accompanied by contraction. Furthermore water starts to expand 4° C. above its freezing point. The expansion may be due to the formation of H_4O_2 molecules, a process which goes forward as water is cooled. (See Mellor, Comprehensive Treatise, Vol. 1, page 411.)

of all substances. In the same way there must be a definite temperature at which the kinetic energy becomes so small that the attractive forces pack the molecules into the definite arrangements characteristic of the solid state; this temperature is called the **freezing point** of the substance.

Forms of Crystals.—There can be only one kind of gaseous form and only one kind of liquid form because in both of these states the molecules are more or less free to move about. When a substance assumes the crystalline or solid form, the molecules are packed in such definite arrangements that their motions are very much restricted and that the relative positions of the molecules within the substance are very definitely fixed. Now there are many different ways in which molecules may arrange themselves in order to achieve the close-packed arrangement of the crystalline state. The result is that there are many different forms of crystals. Some are cubes, some long and needle-like, and there are many other forms. The crystalline form is another characteristic property of the substance by means of which, when in a solid state, it can be distinguished from other substances. The study of these crystalline forms is an important one from both a practical and a theoretical aspect. It is discussed further on page 351.

In this chapter the modern view with regard to the structure of matter has been presented. The molecular theory makes the mechanism of chemical reactions easier to understand because it tells us that reactions take place between small particles of matter rather than between large bodies. The supposition that molecules are moving about explains how they come into contact with one another and how reactions occur.

Although the molecular theory makes clearer the mode of chemical reaction, it cannot explain why certain substances react with some substances and not with others. As a matter of fact, chemists have not yet arrived at a satisfactory explanation of this phenomenon; but they have made rapid strides in that direction, especially in the last few years. In order to learn something of what has been done the structure of molecules must next be studied.

EXERCISES

(1) (*a*) What is the exact meaning of the symbol, v, in the equation $p \times v = w \times T \times$ (constant)? (*b*) What is meaning of the symbol as it is actually used in most calculations? (*c*) What effect does this use of the symbol have on the value of the product, $p \times v$, compared to its value according to the kinetic theory? (*d*) Are molecules readily compressible? (*e*) Why is the effect noticeable only at high pressures?

(2) (*a*) What effect does the existence of attractive forces between the molecules have upon the pressure they actually exert compared to the pressure they ought to exert according to the kinetic theory? (*b*) How, therefore, does the attractive force affect the values of the product, $p \times v$? (*c*) Why is this effect noticeable chiefly at high pressures? (*d*) Why is it more noticeable at low temperatures than at high ones?

(3) Explain why in the case of carbon dioxide the value of the product $p \times v$ first decreases and then increases as the pressure is increased.

(4) What evidence is there to show that the attractive forces between molecules depend on the nature of the molecules?

(5) (*a*) Define the term "critical temperature." (*b*) Explain the significance of the critical temperature from the point of view of the kinetic theory.

(6) What picture of the process of solidification is given by the kinetic theory?

(7) (*a*) Are the molecules of liquid and solid substances in motion? (*b*) If they are in motion, compare the kinetic energy of the molecules of a given substance at a given temperature when the substance is gaseous, when liquid and when solid. (Before answering the question, consider carefully what was said about the relationship between kinetic energy and temperature in Chapter II, page 22.)

REFERENCES

Mellor—Comprehensive Treatise, Vol. I, Chapter IV, sections 3 and 7, deal with deviations from the gas laws. Chapter XI of the same volume takes up crystals but is very detailed. References to crystal structure are found in Chapter XXIII.

Alembic Club Reprint Number 12—Liquefaction of Gases. Faraday. (1823–1845.)

CHAPTER IV

THE ATOMIC THEORY

The Law of Simple Multiple Proportions—Preliminary Discussion of the Structure of Atoms

Substances are characterized and identified not only by their physical properties and chemical reactions, but also by definite composition. Thus, sodium chloride always contains 1.541 grams of chlorine for every gram of sodium, whether the salt is obtained from natural sources or is prepared in the laboratory, and irrespective of the method of analysis or of the temperature or other conditions under which the analysis is made. There are cases, however, in which two elements combine with each other in more than one proportion. If lead is heated at 500° C. in air for a considerable length of time, a red powder called minium, or red lead, is obtained. Analysis of the product shows it to be a compound of lead and oxygen containing 90.67 per cent of the former and 9.33 per cent of the latter. In other words, for every gram of oxygen there are 9.71 grams of lead. If, on the other hand, the lead is heated in air at a higher temperature (750° C.), a yellow powder, called litharge, is formed. This also is a compound of lead and oxygen, but it contains 92.83 per cent of lead and 7.17 per cent of oxygen, or, for each gram of oxygen there are 12.94 grams of lead. Under other experimental conditions, a brown substance, known as lead dioxide, which also contains oxygen and lead may be prepared. In this compound the weight of lead per gram of oxygen is 6.469 grams.[1]

[1] The fact that, in these various ways of making substances by the combination of lead and oxygen, the two elements combine in different proportions does not at all mean that this behavior is an exception to the definition for a substance; it means, by the very implication of that definition, that under the different external conditions of temperature different substances are formed. This view is borne out by the fact that in the one case the substance obtained is red, in the second yellow, and in the third brown.

The Law of Multiple Proportions.—The phenomenon that two elements combine in more than one proportion is a very common one in which there is one significant point that may be illustrated by means of the data given above. The amount of lead combined with 1 gram of oxygen in minium is practically 1.5 times the amount of lead combined with the same weight of oxygen in lead dioxide, and the weight of lead per gram of oxygen in litharge is exactly twice that in lead dioxide. These relations may perhaps be made clearer by restating them as follows: the weights of lead which combine with 1 gram of oxygen in the three compounds, lead dioxide, minium, and litharge, are respectively 2×3.234, 3×3.234 and 4×3.234 grams. The reappearance of multiples of the number 3.234 is not likely to be merely accidental, and the fact that **whenever two or more elements form more than one compound with one another, their proportions in the different compounds are always simple multiples of each other,** as in the three oxides of lead, makes it quite certain that the phenomenon is not a mere coincidence. The statement in heavy type is called the law of **simple multiple proportions.** Its significance may be made clear more easily if the generalized law is restated as follows: If in one compound of two elements the weights of the elements are to one another as x is to y, then in any other compounds formed by these same two elements, the weights of the two will be in the ratio x to $2y$, or x to $3y$ or some other simple multiples of x and y.

The Atomic Theory.—Facts of such universal truth as the laws of definite composition and of simple multiple proportions must have a deeper significance for which the chemist must attempt to find a satisfactory interpretation. In this instance the facts themselves suggest that **the elements, of which the molecules are composed, are present in the molecules in aggregates of definite weight. These small particles** of which the molecules are thus supposed to be built are called **atoms.** If each molecule of sodium chloride is built up of a definite number of sodium and chlorine atoms, and if all sodium and all chlorine atoms have a definite weight, the ratio of the weight of sodium to that of chlorine must be the same in all molecules of sodium chloride, and consequently in all samples of sodium chloride.

According to the atomic theory, atoms might combine with one another in more than one way to form molecules. Thus 1 atom of the element A might combine with 1 or 2 or 3 atoms of B, etc., or 2 atoms of A might combine with 3 of B, and so on. Each of the different ways of combining leads to a different sort of molecule, and to a different substance. But since the atoms of any given element are all supposed to have the same weight, the molecules (and hence, also the substance) which contain 2 atoms of B for every one of A must contain twice as much of the element B by weight as do those which consist of only 1 atom of each element per molecule. Similar relations between the weights of the two elements in other substances, resulting from other possible ways in which the atoms may be supposed to combine, can be worked out. But these weight relations are exactly those which exist in fact, and are summarized in the law of simple multiple proportions. None other than these simple relations in the weights of the elements of the different compounds is possible as long as it is assumed that the atoms always enter into the compounds as whole atoms, and not ever in fractional parts of an atom.

Importance of the Atomic Theory.—The weight relations characteristic of chemical combinations, as summarized in the fact of the definite composition of substances and in the law of simple multiple proportions, have led to the acceptance of the atomic theory. This theory is corroborated by a large number of other facts of chemistry and physics, some of which will be dealt with later, and has become the foundation stone of all chemical theory. The atomic theory, in addition to giving a very simple and satisfactory interpretation of these weight relations, also enables the chemist to picture to himself how the molecules are built up from the atoms. In the field of organic chemistry it frequently happens that two or more compounds have exactly the same composition. The atomic theory has been expanded to explain this fact by assuming that the difference between these substances lies in a difference in the arrangement of the atoms within the molecule. By long experimentation and very skillful reasoning, chemists have been able to obtain a fairly reliable picture of what these arrangements probably are.

This study has led to the remarkable developments of the last fifty years, in the chemistry and manufacture of dyes, explosives, and synthetic drugs.

Structure of Atoms.—Although the atomic theory has, in this way, been of the greatest importance in furthering the advance of chemical thought and knowledge, there is one respect in which it has been unable to shed light on what is probably the most fundamental question the science has to answer. The atomic theory makes it easy to understand how combination between elements occurs, and to picture the architecture of the resulting molecule. But it does not in the least explain why some pairs of atoms combine with each other, whereas other pairs of atoms do not. The search for an answer to this problem has been very fascinating. Until a few years ago, it was entirely unsuccessful. The developments of recent years have not completely solved the problem, but they have at least shown in what direction the solution may ultimately be found. Chemists and physicists have recently begun to search for the answer by attempting to study the structure of atoms. A preliminary description of some of the newer facts and of the conclusions drawn from them will be of interest now, even though more detailed discussion will have to be deferred to a later chapter.

Cathode Rays and Electrons.—When an electric discharge is passed through a highly evacuated glass tube, a peculiar phenomenon known as the "cathode rays" is observed. These rays seem to consist of a greenish opalescence passing through the tube. A piece of metal, such as platinum, placed in their path becomes heated, and may be raised to so high a temperature that it glows. Another striking phenomenon is observed when the tube is placed between two metallic plates one of which carries a heavy positive and the other a heavy negative charge of electricity. Under these conditions the ray of opalescence is always deflected toward the positive plate. When it is bent from its direct path through the tube, the ray strikes the sides of the glass vessel, and where this occurs the opalescence is greatly intensified. The heating of a piece of metal inserted in the path of the ray suggests that these rays may consist of very small particles moving with such enormous velocity that, when they

strike the metal, a relatively large amount of heat is generated. On the other hand, the deflection toward the positive plate makes inevitable the conclusion that such particles, if they do exist, are negatively charged. By measuring the deflection and by other experiments, it has been possible to determine both the mass and the charge such particles must possess in order to explain their behavior in the tubes.

These experiments have led to the most fundamental results, for it has been found that the mass and the charge of these negatively charged particles are the same under all conditions. A moment's consideration of their origin makes clear the significance of this result. The particles can come only from sources within the tube—either from the electrode, or from the small amount of gas which is always left in the tubes. Regardless, therefore, of the nature of these electrodes or of the kind of gas, minute particles possessing identical properties are always obtained. From this fact there can be drawn but one conclusion—namely that, under the influence of the electrical discharge, the gases or the electrodes, whichever the case may prove to be, are decomposed into negatively charged particles, and that, therefore, the atoms which constitute the electrodes or gases must be decomposed also. The atoms thus appear to be constructed of still smaller units which are negatively charged and have been called **electrons.**

Radioactivity and the Structure of Atoms.—Another and an entirely different field of investigation has brought further corroboration and extension of the electron theory of matter. It is now known to everyone familiar with the recent developments of chemistry that there are certain elements characterized by very unusual behavior. One of these elements is **radium.** Their peculiar property is that they spontaneously give out rays of extraordinarily penetrating qualities. These rays are of three kinds, alpha, beta and gamma. The alpha rays are the least penetrating and are due to the ejection from the mass of the radioactive material [1] of relatively slow moving and relatively heavy positively charged particles. The beta rays consist of very light, rapidly moving particles identical with the electrons.

[1] See page 5.

Gamma rays are similar to light rays, but of extremely short wave lengths. They are caused by the impact of alpha and beta rays upon the residual mass of material, and are similar in character to X-rays.

These phenomena and others to be discussed later (Chapter XXIV) have led scientists to the conclusion that atoms consist of a relatively heavy, positively charged nucleus surrounded by negatively charged electrons. It is now quite well established that the chemical properties of the atoms depend on the number of electrons around the nucleus. Since atoms are electrically neutral, the total charge on the electrons must be equal in magnitude to the charge on the nucleus; this charge, must, therefore, determine the number of electrons in the outer part of the atom, and thus its properties. The charge on the nucleus is, in turn, directly related to its mass, and consequently to the mass of the atom, for electrons are so light that they contribute only an inappreciable amount to the total weight.

The weights of the atoms thus contain the whole story of chemistry. All of the connections are not yet clear, but the day may come when the behavior of all of the elements may be predicted and the composition and properties of all of their compounds foretold from these quantities. Although the subject of atomic weights may at first glance seem to be dry and formal, and to deal only with abstract numerical relations, it really is the key which unlocks the door to a world of interesting facts and speculations. The initial presentation of atomic weights is taken up in the next chapter. Their full significance will appear as the subject as a whole unfolds. (See particularly Chapters XXII, XXIII and XXIV.)

EXERCISES

(1) Manganous oxide contains 77.45 per cent of manganese and 22.55 per cent of oxygen, manganic oxide 69.59 per cent and 30.41 per cent, respectively, and manganese dioxide 63.19 per cent and 36.81 per cent respectively of the two elements. Show from these data that the amounts of the elements in the three compounds bear the relationship expressed in the law of multiple proportions. (Note.—Use the method employed in the text on page 40.)

(2) Explain how the atomic theory accounts for the weight relationship illustrated by the preceding problem.

(3) (*a*) What is the evidence that the cathode rays are due to small, negatively charged particles? (*b*) What is the evidence that the particles of the rays are always of the same kind?

(4) Describe all of the phenomena, thus far mentioned in the text, characteristic of the behavior of radioactive substances. (Include the facts mentioned in Chapter I, page 5.)

(5) What conclusions have been drawn from the study of cathode rays and of the products of radioactive changes?

(6) (*a*) According to the hypothesis outlined in this chapter, concerning the structure of atoms, what directly determines the chemical and physical properties of the atoms? (*b*) Assuming that the hypothesis is correct, why should there be a relationship between chemical properties of elements and the weights of their atoms?

REFERENCES

An interesting though rather brief account of the atomic theory is found in Moore, History of Chemistry, Chapter VIII. A more detailed discussion is given in Lowry, Historical Introduction to Chemistry, Chapters XIV and XV. References on structure of atoms are given in Chapter XXIV. For early papers, see Alembic Club Reprint, Number 2, Foundations of Atomic Theory; Papers by Dalton, Wollaston and Thomas Thomson (1802–1808).

CHAPTER V

MOLECULAR AND ATOMIC WEIGHTS

Avogadro's Law.—Rule of Dulong and Petit

Early in the nineteenth century an Italian chemist, Avogadro, advanced the hypothesis that **equal volumes of gases at the same temperature and pressure contain equal numbers of molecules** irrespective of the nature of the gaseous substances. Although for more than fifty years practically no attention was paid to this principle, it has now become one of the most firmly established laws of chemistry and physics. Its acceptance was so long delayed because the chemical evidence lies largely and most clearly in the field of organic chemistry. At the time of Avogadro this branch of chemistry was quite undeveloped, and the experimental material upon which he based his deductions was too meager to impress other chemists. It is impossible to give here the chemical evidence upon which the theory is based, because for an understanding of these proofs some knowledge of organic chemistry is necessary.[1] In recent years Avogadro's law has received decided corroboration from new developments in the field of physics, and it is desirable, at this point, to describe some of this physical evidence although the underlying theory is too complex to be presented in detail.

The Brownian Movement.—With water or other liquids certain substances, such as gelatine, are capable of forming mixtures which are called colloidal and have superficially the appearance of solutions.[2] On closer observation colloidal mixtures are found to differ in many essential respects from true solutions. They are, in fact, suspensions from which the suspended material does not settle out. The suspended particles can, in many cases, be seen through the microscope or detected by

[1] See however, page 69.

[2] Chapter XXIX.

an instrument called the ultramicroscope. They are extremely minute and in continuous motion—a phenomenon discovered by R. Brown, after whom it has been called the "Brownian Movement."

The motions of the suspended particles resemble in many ways the picture which the kinetic theory gives of the

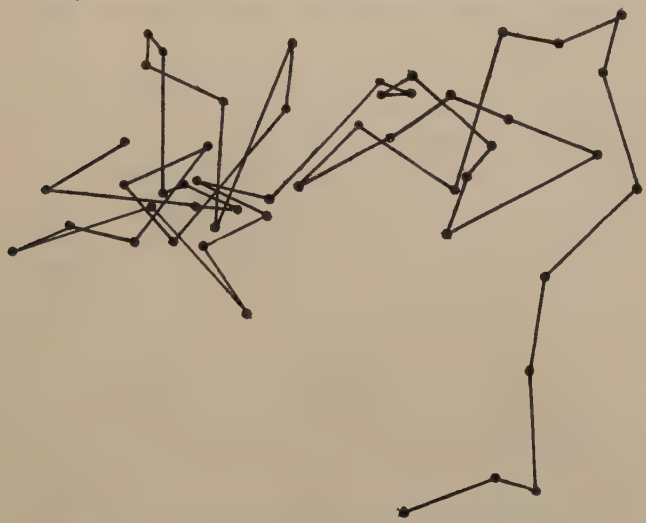


FIG. 3.—THE PATH OF A SUSPENDED PARTICLE.

This figure shows the effect of impacts by molecules of solvent on the direction of motion.

motions of molecules. The phenomenon is explained roughly as follows: A particle suspended in water, must, every now and then, be struck by some one of the many water molecules which according to the kinetic theory are always moving about at relatively high speed. If the particle struck is not too large, it is set in motion by the impact. Before it has moved very far it will be struck by another water molecule, and the direction of the motion will be changed. In this way the particle is kept moving up and down, forward and back, to one side and the other. If its path were traced during a measurable period of time, a very complex figure consisting of many straight lines crossing and recrossing each other many times, would be obtained (Fig. 3).

What is thus pictured for any one particle is, of course, likewise the history of any other suspended particle. Such a complex phenomenon does not seem likely to lend itself to exact mathematical analysis, but the famous physicist, Einstein, has succeeded in showing that the average displacement of a particle, in a given direction for a known period of time in a medium of given properties, varies with the kinetic energy of the particle.

By making use of the Einstein equation for this relationship, it has been possible to measure the mean kinetic energy of such colloidal particles, and to show that, irrespective of the nature of these particles, their mean kinetic energy depends only on the absolute temperature. This fact may now be applied to the equation, $p = \frac{1}{3}nmu^2/v$, for the pressure of a gas, which was developed in Chapter II from the kinetic theory. This equation may be rewritten as follows: $p \times v = (\frac{2}{3}n) \times (\frac{1}{2}mu^2)$. The expression, $\frac{1}{2}mu^2$, represents the mean kinetic energy of the molecules. If, therefore, two gaseous substances have the same volume (v) and the same pressure (p) and if, at a given temperature, the mean kinetic energy of the molecules is also the same for the two substances it is evident that the remaining term of the equation, namely n the number of molecules, must be the same for the two substances. This, however, is Avogadro's law, for its says that the number of particles does not depend upon the nature of the substance but only on the temperature, the pressure and the volume.

The same method of investigation has been applied by Millikan to the study of the movements of oil drops suspended in air and other gases, and he has arrived at the same conclusions drawn from the study of suspensions of colloidal particles in liquids. These investigations have gone further, for it has been possible from them actually to calculate **the number of molecules** which are contained in a given volume of any gas at any temperature or pressure, provided the gas obeys the gas laws. The number thus found, for a volume of one liter at 0° and 760 mm., is 2.7×10^{22}. 2.7×10^{22} represents simply another way of writing 27,000,000,000,000,000,000,000. This is so large a quantity that it is really impossible to picture it. The following

analogy may help impress its significance. It has been calculated that the number of molecules in one cubic centimeter of gas at standard conditions is approximately the same as the number of particles of sand in a volume one mile long, one mile wide and one mile deep.[1]

There have been other methods devised for determining the number of molecules in a liter of gas at standard conditions, but they will be mentioned only very briefly. Thus it has been possible to determine the quantity of electricity carried by a single electron and, from this quantity, the number of molecules per unit volume. An investigation of the blue color of the sky has led in still another way to a calculation of the same number, and all of these different methods have given results which agree excellently with the value stated in the preceding paragraph. This agreement between numbers obtained by studying the motions of particles suspended in liquids, and of oil drops suspended in air, by measuring the charge on an electron, by examining the blue color of the sky—experiments in fields so widely different that they could hardly be supposed to have any connection—appeals to the imagination as one of the most wonderful achievements of modern science. It is this achievement which has made universal the acceptance of Avogadro's hypothesis as a law of nature.

Methods for Determining the Weight of Molecules.—Avogadro's Law and the determination of the actual number of molecules contained in 1 liter open the way to two methods of determining the weights of different kinds of molecules. Since it is known that in 1 liter at standard conditions there are 2.7×10^{22} molecules, the weight of 1 liter of any gas at these conditions can be measured. This weight, divided by the number of molecules, per liter, gives the weight of 1 molecule of the substance. For example, 1 liter of hydrogen gas weighs 0.08987 gram. Dividing this by 2.7×10^{22} gives for the weight of 1 molecule of hydrogen 3.3×10^{-24} which means

$$\frac{3.3}{1{,}000{,}000{,}000{,}000{,}000{,}000{,}000}$$

[1] McCoy and Terry, Introduction to General Chemistry (1920), page 114.

This method is not used by the chemist for two reasons. In the first place the weight of a molecule of hydrogen in grams is so small that it is very inconvenient to use. The second reason is that, although the number of molecules per liter of a gas has been determined with an accuracy of from 0.1 to 0.2 per cent (which is remarkable in view of the difficulty of the measurement) this method is not nearly so accurate as the one described below.

Units for Weights of Molecules.—Before describing the second and generally adopted method for obtaining molecular weights, a word must be said about the units employed in expressing weights in general. Everyone is familiar with the fact that there are many such units in common use. In the United States the ounce, the pound, the ton and other units are employed commercially. The unit used for any particular purpose is so chosen that the number representing the weight is neither inconveniently large nor inconveniently small. If a person goes to the grocery store to buy sugar, he asks neither for $\frac{1}{4000}$ of a ton nor for 80 ounces, but for 5 pounds. On the other hand, if he is laying in a winter's supply of coal he does not ask for 30,000 pounds, but orders 15 tons. In scientific work the gram, the kilogram and the milligram are the customary units. Probably, all units of weight originally represented the weight of some common object to which all others were compared. Thus, the statement that an object weighs 100 grams means that it weighs 100 times as much as 1 c.c. of water at 4° C.

In choosing a unit in which the weights of molecules may be conveniently expressed, a difficulty is met because there is no common object weighing little enough to use as a comparison standard. Chemists have, therefore, adopted the device of expressing the weights of molecules and of atoms in terms of the weight of some one molecule. This, at least, is the principle of the method; for reasons which will appear later it has been slightly modified. The unit actually chosen is such that 1 molecule of oxygen gas weighs 32 times as much as the unit. For most units some name, such as pound, is in general use, and the suggestion was once made to call the unit for weights of molecules and atoms the "Stas," in honor of one of the first

investigators to determine these quantities accurately. But this suggestion and others of similar nature have met with little favor; common usage at present is to say simply that an atom or a molecule weighs a certain number of "units," or more generally to leave out even the word "unit" and to give only the number. Thus when the weight of a molecule of oxygen gas is given as 32, 32 "units" is meant.

Determination of Molecular Weights.—The method for determining molecular weights may now be developed. If 1 liter of a gaseous substance, X, weighs W grams at S. C., the weight of each molecule of the substance is $W/(2.7 \times 10^{22})$ grams. The weight of 1 liter of oxygen gas at S. C. is 1.429 grams; the weight of 1 molecule of oxygen gas is, therefore, $1.429/(2.7 \times 10^{22})$ grams since, according to Avogadro's law, all gases at S. C. contain 2.7×10^{22} molecules. Hence:

$$\frac{\text{the weight of 1 molecule of } X}{\text{the weight of 1 molecule of oxygen}} = \frac{W/(2.7 \times 10^{22})}{1.429/(2.7 \times 10^{22})}$$

The somewhat inaccurate number, 2.7×10^{22} cancels out of the equation. As we have developed the latter, the weight of the molecules of X and the weight of the oxygen molecules are given in terms of grams. But the ratio of the two weights is the same no matter in what units those weights are expressed, provided the same unit is used for both, and it is therefore permissible to express both of them in the unit chosen as described above. The "weight of 1 molecule of oxygen" in these terms is 32 units and, by clearing the left side of fractions, the equation becomes

the weight of 1 molecule of $X = (W/1.429) \times 32$ "units."

or

the weight of 1 molecule of $X = W \times 32/1.429$ "units."

The last equation means that in order to determine the weight of a molecule of any gaseous substance, the weight, (W), of 1 liter of the substance at standard conditions is multiplied by 32 and divided by 1.429. Since it is necessary for every such determination to multiply by 32 and divide by 1.429, it is convenient to carry that step out once for always. $32/1.429 = 22.4$. Hence the equation finally becomes:

the weight of 1 molecule of $X = W \times 22.4$ "units."

W is the weight of 1 liter; another and a more convenient way of saying "22.4 times the weight of 1 liter" is "the weight of 22.4 liters." A very simple definition has been thus reached —the **weight of the molecule of any gaseous substance, in terms of the unit chosen, is a number equal to the weight in grams of 22.4 liters of that substance at standard conditions.** The weight of 1 molecule **in the unit chosen,** is called the **molecular weight** of the substance; the weight **in grams** of 22.4 liters, to which the molecular weight is numerically equal, is called the **gram molecular weight.**

There are several points to which the student's attention is once more called. The unit which has been chosen to express the weights of molecules and atoms is an arbitrary one, devised for certain reasons of convenience which will become clear when the question of atomic weights has been taken up. By the choice of the unit so that 1 molecule of oxygen is said to weigh 32 of them, and from the fact that 1 liter of oxygen gas weighs 1.429, the quantity 22.4 liters enters into the method for molecular weight determinations. There is nothing fundamental about the volume 22.4 liters; nevertheless, since it is always used in molecular weight determinations and other chemical calculations, it has been called the "chemical unit volume." For convenience, the number of molecules contained in this volume at 0°, 760 mm., 6.06×10^{23}, is generally denoted by the letter N, and is called **"Avogadro's number."**

It is to be noted, further, that in the method described for determining the molecular weights of gaseous substances no chemical property is involved—the only measurement required is the weight of the gas at a given volume, temperature and pressure. The determination of atomic weights, on the other hand, involves the study of the chemical composition of a large number of substances. The atomic weights, therefore, are constants of far greater interest to the chemist than are the molecular weights.[1]

Principle of the Method for Determining Atomic Weights.— In the description of the facts upon which the atomic theory is

[1] The student is advised to interrupt his reading at this point in order to review the material thus far presented in this chapter. Exercises 1–10, page 62, will be of service in this connection.

based, it was pointed out that the law of multiple proportions may be explained in a simple way on the assumption that atoms combine with different numbers of other atoms to make compounds. Suppose that there is an element, E, which forms a large number of gaseous compounds. The most reasonable assumption to make with regard to these compounds is that they do not all contain the same number of atoms of E per molecule. There should be some compounds which contain 1 atom of E per molecule, others which contain 2 atoms of E per molecule, still others which contain 3 atoms of E per molecule, and so on. But there can be no compounds whose molecules will contain any fractional number of atoms, because, according to the atomic theory, the molecules contain the elementary substances as whole atoms only.

From this discussion it is at once seen what the number of atoms of E per liter of these various gaseous compounds of E at standard conditions must be. Since this volume of a gas always contains the same number of molecules, 2.7×10^{22}, the number of atoms of E contained per liter will be 2.7×10^{22}, or 2.7×10^{22} times 2 or 3 or any other whole number, but never any fractional number. If the weight of an atom of E is m grams, the weight of the element E in 1 liter of the gaseous compounds will be $(2.7 \times 10^{22}) \times m$ in those compounds which contain only 1 atom of E per molecule, or 2 or 3 or some other whole number times the quantity $(2.7 \times 10^{22}) \times m$ grams, in the other kinds of compounds mentioned. If this line of reasoning is correct the weight of an element, contained in 1 liter of any of its gaseous compounds at standard conditions, should be some smallest or "minimum" weight or some integral multiple of this minimum weight. A table follows which gives the necessary data for comparing the theory with actual data for several elements.

The table shows that the weight of hydrogen per liter of its gaseous compounds is either very nearly 0.045 gram or very nearly 2 or 3 or some other whole number times 0.045 gram; that the weight of carbon per liter of the various carbon compounds, for which the data are given in the table, is either very nearly 0.54 gram or some whole number times 0.54 gram; that

TABLE I

MINIMUM WEIGHTS IN GRAMS (PER LITER) AND THEIR MULTIPLES, CALCULATED FROM THE WEIGHTS IN GRAMS (PER LITER AT 0°, 760 MM.) OF VARIOUS GASEOUS COMPOUNDS AND THEIR PER CENT COMPOSITION.

Name of the Compound	Actual Weight of 1 Liter of the Gas at S. C.	Weight of 1 Liter at S.C. Corrected for Deviations from Gas Laws	Per Cent Composition	Actual Weight of Hydrogen per Liter	Weight of Hydrogen in Multiples (approx.), of Minimum Wt.	Actual Weight of Carbon per Liter	Weight of Carbon in Multiples of Minimum Weight	Weight of Oxygen per Liter	Weight of Oxygen in Multiples of Minimum Weight
Hydrogen chloride	1.639	1.628	H 2.76 Cl 97.24	0.0453	0.045×1				
Hydrogen bromide	3.644	3.613	H 1.25 Br 98.75	0.0453	0.045×1				
Hydrogen gas	0.0899	0.0839	H 100	0.090	0.045×2				
Acetylene	1.180	1.160	H 7.45 C 92.55	0.0914	0.045×2	1.08	0.54×2		
Ammonia	0.771	0.764	H 17.48 N 82.52	0.137	0.045×3				
Methyl chloride	2.304	2.254	H 5.99 C 23.77 Cl 70.24	0.138	0.045×3	0.548	0.54×1		
Methane	0.717	0.716	H 25.14 C 74.86	0.180	0.045×4	0.537	0.54×1		
Ethane	1.356	1.342	H 20.13 C 79.87	0.273	0.045×6	1.083	0.54×2		
Propane	2.014	1.968	H 18.29 C 81.71	0.361	0.045×8	1.66	0.54×3		
Iso-pentane	3.34	3.22	H 16.77 C 83.23	0.56	0.045×12	2.78	0.54×5		
Carbon monoxide	1.250	1.250	C 42.88 O 57.12	.....	.....	0.546	0.54×1	0.714	0.714×1
Carbon dioxide	1.977	1.965	C 27.29 O 72.71	.....	.....	0.539	0.54×1	1.438	0.714×2
Oxygen gas	1.429	1.429	O 100	.....	.....	.....	.....	1.429	0.714×2

NOTE TO THE TABLE.—All of the substances are measured at standard conditions except iso-pentane, for which the data are calculated from values obtained at 100° C. Comparison of the second and third columns gives an idea of the magnitude of deviations from the gas laws. The greatest deviation is in the case of iso-pentane, which is the substance of highest boiling point. The data of the last six columns are explained in the text.

the weight of oxygen in the various oxygen compounds is either 0.714 gram or some whole number times this weight. The weights are not always exactly integral multiples of the smallest weight because the various gaseous substances for which the data have been given do not strictly obey the gas laws, and hence the number of molecules per liter is not exactly the same in all of them. When the weights per liter are corrected for these deviations from the gas laws it is found that all of the weights are **exact** multiples of the smallest weight for each atom. What has been predicted from the atomic theory is, therefore, corroborated by experiment.

The method for determining the atomic weights is now very similar to the method for calculating molecular weights. Of a series of gaseous compounds of a given element, those which contain the minimum weight of the element per liter (at standard conditions, corrected for deviations from the gas laws) are the ones which contain but 1 atom of the element per molecule. Consequently the number of atoms per liter in such compounds is 2.7×10^{22} since there are 2.7×10^{22} molecules per liter. If this minimum weight of the element is, let us say, A grams,[1] the weight of each atom must be $A/(2.7 \times 10^{22})$ grams. In the discussion of molecular weights it was shown that the weight of 1 molecule of oxygen is $1.429/2.7 \times 10^{22}$ grams. Hence:

$$\frac{\text{the weight of 1 atom of } E}{\text{the weight of 1 molecule of oxygen}} = \frac{A/(2.7 \times 10^{22})}{1.429/(2.7 \times 10^{22})}$$

Although the weight of 1 liter of oxygen (1.429 grams) and the minimum weight of the element in its various gaseous compounds per liter are expressed in this equation in grams, it is evident again that the **ratio** of the weights is the same for any system of weights used, provided that the weights of 1 atom of E and of 1 molecule of oxygen are expressed in the same units. It is therefore possible to express both of the latter quantities in terms of the arbitrary unit chosen for molecular weights. If this is done the weight of 1 molecule of oxygen is 32, the number

[1] $A = (2.7 \times 10^{22}) \times m.$

2.7×10^{22} of course cancels out of the equation, and the latter becomes:

$$\text{the weight of 1 atom of } E = A \times 22.4 \text{ "units."}$$

Translated into words, the last equation states that **the weight of an atom of an element, expressed in the unit chosen, is numerically equal to the smallest weight of the element ever found in 22.4 liters of any of its gaseous compounds at standard conditions.**[1] The weight of 1 atom of an element expressed in the units chosen is called the **atomic weight** of the element, and the weight of N atoms (the minimum weight found in 22.4 liters of any of its compounds) is called the **gram atomic weight.**

Procedure for Atomic Weight Determinations.—According to the method outlined above, the following procedure has to be carried out for the determination of the atomic weight of an element. The first step is to prepare, in as pure condition as possible, a large number of gaseous compounds of the element.[2] The weight in grams of a measured volume of each of these gases or vapors is accurately determined at a measured temperature and pressure. The volume is then corrected to 0° and 760 mm., taking into account deviations from the gas laws. From this corrected volume the weight of 22.4 liters at standard conditions is calculated. Next the per cent of the element contained in each of the compounds is determined by analysis. **From the weight of 22.4 liters and the analytical data, the weight in grams of the element contained in this volume of each of the compounds is calculated. The smallest of these weights is, presumably, a number equal to the atomic weight.** This method assumes that among the compounds chosen there is at least one whose molecules contain but 1 atom of the element. If the number of the compounds studied is sufficiently large, the chances are very great that such a compound is in the group.

[1] It has been pointed out above that the volume of the compounds must be corrected for deviations from the gas laws.

[2] It is frequently difficult to find enough compounds which are gases at ordinary temperatures. This difficulty can be avoided by using compounds which are volatile at temperatures not too high to make accurate measurements.

But there is another way of making sure that this is actually the case.

Suppose that there is in the group studied no compound the molecules of which contain only 1 atom of the element. Assume further that the compound which has the smallest number of atoms of the element per molecule is one with 2 atoms of the element in each molecule. If this is the case, compounds containing 3 or 5 or some other odd number of atoms per molecule, must contain 1.5 or 2.5 or some other fractional number times the weight of the element in the compound which contains only 2 atoms per molecule. But the weights of the element in its various gaseous compounds must be either a minimum value or some **whole number** times this minimum value, in order that the latter should correctly represent the atomic weight. In the imaginary case just discussed, this is not true, and the smallest weight is, therefore, not the real "minimum weight" as that term has just been used. Evidently in such a case the atomic weight must be a number which is a divisor of all of the weights of the element actually found, by experiment, in 22.4 liters of all of its gaseous compounds at standard conditions. The definition of the atomic weight may, therefore, be altered somewhat to fit the hypothetical case just discussed. This may be done by saying that **the atomic weight of an element is a number which is the largest common divisor of the weights of that element ever found in 22.4 liters of any of its gaseous compounds at standard conditions.**[1]

Rule of Dulong and Petit.—One might naturally ask how to determine the atomic weight of an element which forms no gaseous or volatile compounds or is a constitutent of so few such compounds that even the determination of the largest common divisor has no real significance. In that case an empirical rule discovered by Dulong and Petit is sometimes useful. They found that when the atomic weights of elements are multiplied by the specific heats of the elementary substances in the solid condition, the products are very nearly the same in almost all cases.[2] The following table gives some illustrations of this rule.

[1] Deviations from the gas laws must be taken into account.

[2] A definition of the term "specific heat" is given on page 86.

TABLE II

SPECIFIC HEATS OF SOME OF THE ELEMENTS IN THE SOLID STATE
(To Illustrate the Rule of Dulong and Petit)

ELEMENT	SPECIFIC HEAT	ATOMIC WEIGHT	(ATOMIC WEIGHT × SPECIFIC HEAT)
Aluminium	0.217	27.0	5.86
Antimony	0.050	120.2	6.01
Boron	0.307	10.9	3.35
Calcium	0.149	40.07	5.97
Copper	0.093	63.57	5.91
Carbon:			
Diamond	0.153	12.0	1.84
Charcoal	0.193	12.0	2.32
Gold	0.032	197.2	6.31
Iron	0.110	55.84	6.14
Sodium	0.295	23.0	6.78
Silicon	0.171	28.1	4.80
Silver	0.056	107.88	6.04
Average (omitting Boron, Silicon and Carbon), 6.1			

Notes to Table II.—Specific heats vary considerably with changes in temperature. Unfortunately data for the same temperature ranges are not obtainable in all cases. In this table the values given are as nearly as possible those for the range from 0° to 100°; that is, the specific heat determined by finding the amount of heat required to warm the substance from 0° to 100° and then dividing this by 100. It is to be noted that only the elements silicon, carbon and boron depart widely from the average value. These three elements are chemically very similar.

The products which should, according to Dulong and Petit's rule be equal to the same number for every element actually differ somewhat, but on the average the product is 6.1 if the elements boron, silicon and carbon, which deviate most widely, are omitted. This rule may then be used for determining approximately what the atomic weight of an element is, but in order to use it for finding the exact atomic weight other data must be taken into consideration. In order to see how this is done an illustration may be used. Suppose no volatile compounds of sodium were known. Its specific heat is 0.29. From the rule one would, therefore, judge that the atomic weight of

sodium should be approximately 6.1/0.29 or 21. Now sodium forms a compound with chlorine, sodium chloride, which contains 23 grams of sodium for every 35.46 grams of chlorine. 35.46 is the atomic weight of chlorine; consequently 35.46 grams of chlorine is the weight of N atoms of chlorine. The number of atoms of sodium which are combined with N atoms of chlorine must be either N or some whole number times N. 23 grams is, therefore, the weight of N or some whole number times N atoms. The atomic weight of sodium is consequently, 23 or some whole number times 23. Application of Dulong and Petit's law has led to the conclusion that the atomic weight of sodium is in the neighborhood of 21. It is clear therefore that 23, and not 2 or 3 or some other whole number times 23, is the exact atomic weight of sodium. There are other ways also in which atomic weights of elements which form no gaseous compounds can be determined. One of these will be described briefly in the chapter on the Periodic System.

In order that the student may become thoroughly familiar with the principles and the methods of determining molecular and atomic weights, he should now work the problems at the end of this chapter.

Table III below gives in the first column a list of the more common elements, in the second column the symbols used to designate them, and in the third column the atomic weights. A complete table of these data for all of the elements whose atomic weights are known is to be found on the inside back cover of this book.

The data in this table make clear why the unit for atomic and molecular weights was chosen of such a value that the oxygen molecule weighs 32 units. In the first place, on this basis none of the atomic weights is a number smaller than one, which is quite convenient. On the other hand, it would have been possible to accomplish the same result by making the weight of the hydrogen atom the unit. At one time atomic weights were actually based on this weight, but the system described in this book was later adopted for two reasons. Accurate atomic weights are calculated from analytical data dealing with the composition of compounds of the various elements. More of

the elements form stable compounds with oxygen than they do with hydrogen, and these compounds are more easily analyzed. Also more of the elements, especially the lighter ones, have atomic weights which are whole numbers, or very nearly whole numbers, when the basis of atomic weight is the molecule of oxygen gas taken as 32 than when the basis is the hydrogen atom.

TABLE III

ATOMIC WEIGHTS AND SYMBOLS OF SOME OF THE MORE COMMON ELEMENTS

Aluminium	Al	26.97	Lithium	Li	6.940
Antimony	Sb	121.77	Magnesium	Mg	24.32
Argon	A	39.91	Manganese	Mn	54.93
Arsenic	As	74.96	Mercury	Hg	200.61
Barium	Ba	137.37	Molybdenum	Mo	96.0
Beryllium	Be	9.02	Neon	Ne	20.2
Bismuth	Bi	209.00	Nickel	Ni	58.69
Boron	B	10.82	Nitrogen	N	14.008
Bromine	Br	79.916	Oxygen	O	16.000
Cadmium	Cd	112.41	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.027
Calcium	Ca	40.07	Platinum	Pt	195.23
Carbon	C	12.000	Potassium	K	39.096
Chlorine	Cl	35.457	Radium	Ra	225.95
Chromium	Cr	52.01	Selenium	Se	79.2
Cobalt	Co	58.94	Silicon	Si	28.06
Copper	Cu	63.57	Silver	Ag	107.880
Fluorine	F	19.00	Sodium	Na	22.997
Gold	Au	197.2	Strontium	Sr	87.63
Helium	He	4.00	Sulfur	S	32.064
Hydrogen	H	1.008	Tin	Sn	118.70
Iodine	I	126.932	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.17
Lead	Pb	207.20	Vanadium	V	50.96
			Zinc	Zn	65.38

Accurate Determinations of Atomic Weights.—Although the method described in this chapter is the fundamental one for the determination of atomic weights, results of the highest accuracy are obtained by analyses of solid or liquid compounds. Large

volumes, which are difficult to manipulate, must be used to obtain accurately weighable quantities of gases. The changes in volume of the latter, due to slight changes in temperature and pressure, and the necessity for making corrections for deviations from the gas laws add to the difficulty of arriving at results of the greatest possible accuracy.

The method for using analytical data of liquids or solids in conjunction with the method described in the text may be illustrated as follows. The analysis of numerous gaseous oxygen compounds has shown that the atomic weight of this element is one-half of the weight of a molecule of oxygen gas; that is, the atomic weight of oxygen is 16. Measurements on the weight of hydrogen in a large number of its gaseous compounds prove that the atomic weight of the element is not far from 1.0. On the other hand, analyses and the determination of the density of gaseous water lead to the conclusion that molecules of the latter consist of 1 oxygen and 2 hydrogen atoms. The most careful analysis of liquid water shows that it contains, for every 16 grams of oxygen, 2.016 grams of hydrogen. From what has been said, it is obvious that the latter quantity is 2 times the gram atomic weight; the atomic weight of hydrogen is, therefore, 1.008. Details of such calculations are, however, best discussed in connection with the analytical methods employed and are, on this account, not taken up in this text.

EXERCISES

(1) State Avogadro's law.

(2) Show that demonstrating the term, $\frac{1}{2}mu^2$, to be the same for all gases at the same temperature is proof of the correctness of Avogadro's law.

(3) Define the term "Avogadro's number."

(4) Why are none of the commonly employed units for weight used to express the weights of atoms and molecules?

(5) What is the basis of the "unit" employed for the weights of atoms and of molecules?

(6) If the weight of 1 liter of a gas at S. C. is X grams, what is the weight of 1 molecule of the gas in terms of grams? (*b*) What, in grams, is the weight of 1 molecule of oxygen? (Express this weight in terms of the

weight in grams of 1 liter of oxygen at S. C.) (*c*) What then is the ratio of the weight of 1 molecule of the gas in grams to the weight of 1 molecule of oxygen in grams? Write the answer to this question in the form of an equation. (*d*) In the equation obtained in *c*, must the weights of the molecules be expressed in terms of any particular unit, as long as both are in terms of the same unit? (*e*) Develop from the equation obtained in *c* another equation which gives the weight of 1 molecule of the gas in terms of the "unit" for molecular and atomic weights.

(7) Show the origin of the number 22.4 used in the statement made on page 52 concerning the molecular weight of a gas.

(8) What is the molecular weight of a gas if 1 liter of it at S. C. (corr.) weighs 2.683 grams?

(9) What is the molecular weight of a gas, if 250 c.c. of it weigh 0.5 gram at 25°, 740 mm.?

(10) What is the weight of 1 liter of a gas at S. C. (corr.) if its molecular weight is 44?

(11) (*a*) If an element forms a large number of gaseous compounds, how can one determine which of these consists of molecules containing but 1 atom of the element per molecule? (*b*) Assuming the smallest weight of an element ever found per liter of its gaseous compounds at S. C. to be *A* grams, write an expression for the weight of its atoms.

(12) After having shown in problem 11 what the weight in grams of an atom of the element is, show what it is when expressed in terms of "units" by comparing the weight in grams of an atom of the element with the weight in grams of 1 molecule of oxygen (as derived in problem 6, *b*.)

(13) An element, *E*, is a constituent of four volatile hydrogen compounds for which the following data, referred to the gaseous condition at S. C. and corrected for deviations from the gas laws, are available:

	Weight of 1 Liter of Compound at Standard Conditions	Per Cent of *E* in the Compound
Compound 1.....	1.250 grams	85.70
Compound 2.....	1.964 grams	81.80
Compound 3.....	0.714 grams	75.00
Compound 4.....	2.588 grams	82.75

(*a*) Show which of these compounds probably contains but 1 atom of the element per molecule. (*Ans.* Compound 3.)

(*b*) What is the atomic weight of the element? (*Ans.* 12.)

(14) An element, *D*, is a constituent of three volatile hydrogen compounds for which the following data, referred to the gaseous condition at S. C. and corrected for deviations from the gas laws, are available:

	Weight of 1 Liter of Compound in Grams	Per Cent of *D* in the Compound
Compound 1.....	1.241	78.43
Compound 2.....	2.393	81.33
Compound 3.....	2.835	85.82

(*a*) Does any one of these compounds contain but 1 atom of *D* per molecule? Give a reason for your answer.

(*b*) What would be the most probable weight per liter, S. C., of the element in a compound which does contain only 1 atom per molecule?

(*c*) Verify the conclusion reached in (*b*) by using the following data: element *D* forms a chloride which contains 9.28 per cent of *D* and weighs 5.236 grams per liter (S. C.).

(*d*) What is the atomic weight of the element?

(15) An element, *F*, is a constituent of the following compounds for which the data, referred to the gaseous condition at S. C. and corrected for deviations from the gas laws, are as given below:

	Weight of 1 Liter of Compound in Grams	Per Cent of *F* in the Compound
Compound 1.....	12.01	20.90
Compound 2.....	4.121	91.33
Compound 3.....	5.460	91.90

Calculate the atomic weight of the element.

(16) The specific heat of an element in the solid state is 0.245. Its chloride contains 25.54 per cent of the element and 74.46 per cent of chlorine. What is the atomic weight of the element? (Hint: Calculate first the approximate atomic weight by the rule of Dulong and Petit. Then calculate the weight of the element combined with 1 gram atomic weight of chlorine. Using the two values thus calculated, judge what is the probable exact atomic weight.)

REFERENCES

The methods by which the correctness of Avogadro's law has been demonstrated and the number of molecules in unit volume of gases determined are described more fully in the following references.

MILLIKAN—New Proofs of the Kinetic Theory of Matter and the Atomic Theory of Electricity. Popular Science Monthly, April and May (1912).

CARTLEDGE—Inorganic Physical Chemistry, pp. 60–64.

WASHBURN—Principles of Physical Chemistry. 2nd edition, pp. 113–117.

J. PERRIN—The Atoms (translated by Hammick), already referred to, is a most interesting book. The first four chapters are of particular interest to students of general chemistry. Chapters III and IV deal with the Brownian Movement.

The actual methods of determining atomic weights with the highest possible degree of accuracy are reviewed in an article of unusual interest by

RICHARDS—Chemical Reviews, Vol. I, p. 1. Pages 1–17 deal with matters discussed in this chapter: the remainder of the article will be referred to in a later chapter.

Richards' work is described also in Cartledge, Inorganic Physical Chemistry, pages 67 to 87. Millard, Physical Chemistry for Colleges, pages 11–17, discusses methods of atomic weight determinations.

CHAPTER VI

SYMBOLS, FORMULAE AND EQUATIONS

The need of symbols and formulae to abbreviate the names of the many substances used and described in chemistry was recognized very early in the history of the science. Even the alchemists made use of them. But since their knowledge of the substances with which they dealt was fairly limited, and their interest in the subject was tinged with mysticism and superstition, the symbols they used did not have any scientific basis.[1] When the difference between compounds and elements had been recognized, the foundation for the modern system of symbols and formulae could be laid. As soon as it was known that common salt is a compound of sodium and chlorine, a formula could be devised which not only is readily recognized by every one familiar with chemistry, but which also gives information about the composition of salt. The substance may be designated by the letters, NaCl, in which Na represents the Latin word "natrium," meaning sodium, and Cl represents chlorine. The system as now used, however, makes each formula a much more complete record of the facts known about the corresponding substance. It is based on the atomic theory of molecular structure, and on the system of molecular and atomic weights which has just been described.

Formulae of Gaseous Substances.—In the discussion of the method for determining atomic weights, it was pointed out that, at any given temperature or pressure, gaseous compounds contain in a given volume either certain minimum weights of each of the constituent elements, or whole numbers times these minimum weights. If the volume chosen is 22.4 liters at

[1] See for examples of such symbols Mellor, Modern Inorganic Chemistry, page 38.

standard conditions, the weights thus found are the atomic weights or integral multiples of them. The symbols of the elements, if they are made to represent gram atomic weights of each, may therefore be used to indicate not only what elements are present, but also how many gram atomic weights of each are contained in the standard volume of gaseous compounds. Thus H_1, H_2, H_3, etc., mean that 22.4 liters of gaseous compounds, in the formulae of which these symbols appear, contain respectively 1.008 grams, or 2×1.008, or 3×1.008, etc., grams of hydrogen at standard conditions. The subscripts must always be whole numbers, since the amounts of hydrogen in the standard volume are always integral multiples of its gram atomic weight, 1.008 grams. Generally the subscript 1 is omitted.

The same system is, of course, used for the other elements also. Thus C represents 12.000 grams of carbon and C, C_2, C_3, etc., mean that the gaseous carbon compounds, represented by formulae in which these symbols appear, contain respectively 12.000 grams, or two, or three, etc., times 12.000 grams of carbon in 22.4 liters at standard conditions. For example, the formula C_2H_6 states that in 22.4 liters of the gaseous compound, ethane, at standard conditions there are two times 12.000 grams of carbon and six times 1.008 grams of hydrogen. It follows that the weight of 22.4 liters of the compound must be $6.048 + 24.00 = 30.048$ grams. The weight of 1 liter, then, is 30.048/22.4 or 1.341 grams. It is likewise possible to calculate from these data the percentage composition. The per cent of carbon is $\left(\frac{24.00}{30.048}\right) \times 100$ and that of hydrogen is $\left(\frac{6.048}{30.048}\right) \times 100$.

But the formula C_2H_6 indicates even more than has been mentioned so far. The discussion of atomic weights brought out the fact that those compounds which contain the gram atomic weight of an element in 22.4 liters at standard conditions have but 1 atom of the element per molecule; that those compounds which contain 2 gram atomic weights in this volume have 2 atoms of the element per molecule, and so on. Hence the subscript numbers used in chemical formulae, though intended to record the experimentally determined number of

gram atomic weights in the chemical unit volume, also indicate the number of atoms per molecule of the compound. Thus the formula C_2H_6 means, in addition to everything already pointed out, that the molecule of ethane consists of 2 atoms of carbon and 6 of hydrogen.

Prefixes.—In writing chemical equations, it is sometimes necessary to indicate that more than the unit volume of the gaseous substance is involved in the reaction. This is done by prefixing the number of volumes used. Thus $2C_2H_6$ means 44.8 liters of ethane at standard conditions, that is, 2×30.048 grams of ethane.

Determination of the Formula of a Gaseous Substance.—When the complete meaning of the formula for a gaseous substance has been grasped, it is easy to understand how such a formula is obtained. Each symbol of the formula represents the number of gram atomic weights of the elements in 22.4 liters of the gaseous compound in question. Therefore, to make the formula of a gaseous substance it is necessary to determine the weight in grams of each element in 22.4 liters of the compound at standard conditions, and then to find the number of gram atomic weights to which this weight corresponds. The only data required are the weight of a known volume of a compound at any known temperature and pressure, the *per cent* of each element in the compound, and the atomic weights of the element. For example, 1 liter of propane at standard conditions (corr.) weighs 1.967 grams. It consists of 18.3 per cent of hydrogen and 81.7 per cent of carbon. The formula is found as follows:

Weight of 22.4 liters of propane $= 1.067 \times 22.4 = 44.06$ grams.
Weight of hydrogen in 22.4 liters of propane $= 44.06 \times 0.183 = 8.06$ grams.
Weight of carbon in 22.4 liters of propane $= 44.06 \times 0.817 = 36.00$ grams.
No. of gram atomic weights of hydrogen per 22.4 liters $= 8.06/1.008 = 8.0$
No. of gram atomic weights of carbon per 22.4 liters $= 36/12 = 3.0$

The formula is, therefore, C_3H_8.[1]

[1] The order in which the symbols are placed in a formula is largely a matter of custom. The positive constituent (see pages 362–367) is usually placed first, but even this rule is not always followed. In carbon compounds, the carbon is generally written first.

Symbols of Some of the Elementary Gases.—The smallest weight of hydrogen ever found in 22.4 liters (corr.) of any gaseous hydrogen compound at standard conditions is 1.008 grams. The weight of 22.4 liters of hydrogen gas itself, however, is 2.016 grams. According to the method just described, the formula of hydrogen gas is determined by dividing the amount of hydrogen in 22.4 liters by the atomic weight. The formula is, therefore, H_2. This formula not only records the weight of 22.4 liters and the amount of hydrogen in this volume, but also implies that there are two atoms of hydrogen in each molecule. Similarly, since 22.4 liters of gaseous chlorine at standard conditions weigh approximately 71 grams, and since the atomic weight of chlorine is 35.46, the formula for chlorine gas is Cl_2. This formula also indicates that there are 2 atoms of chlorine in each molecule of elementary chlorine.

The interesting conclusion just drawn—that the molecules of these elementary substances do not consist of free atoms—is borne out by the following facts. When a given volume of hydrogen unites with an equal volume of chlorine the two yield a volume of gaseous hydrogen chloride just equal to the original volume of the hydrogen plus that of the chlorine. The formula of hydrogen chloride is HCl. The course of this reaction may therefore be indicated as follows:

$$H_2 + Cl_2 \rightarrow 2HCl$$

According to the description of symbols, H_2 represents 22.4 liters of hydrogen at standard conditions, Cl_2 represents 22.4 liters of chlorine, and 2 HCl represents two times 22.4 liters of hydrogen chloride. In this way, then, the equation given is an exact statement of the volume relations actually observed in this reaction.

Suppose for a moment, however, that hydrogen gas did not consist of these molecules, but consisted of hydrogen atoms and that chlorine gas consisted of chlorine atoms. N atoms of hydrogen would then unite with N atoms of chlorine to form N molecules of hydrogen chloride. This could be represented by the equation:

$$N(H) + N(Cl) \rightarrow N(HCl)$$

By Avogadro's law, N particles of hydrogen occupy the same volume as N molecules or free atoms of any other gaseous substance. The equation just written, therefore, implies, if Avogadro's law is correct, that two volumes of the two elements unite to give one volume of hydrogen chloride. The second equation disagrees with the experimental facts, whereas the first one fully agrees with them. The belief, therefore, that gaseous hydrogen and gaseous chlorine contain molecules consisting of 2 atoms of the elements, is justified. In the same way the formulae for oxygen gas and nitrogen gas have been found to be O_2 and N_2 respectively. The formula of gaseous phosphorus is P_4. The formulae of other gaseous or volatile elements will be given when the latter are taken up in detail.

Gay-Lussac's Law of Combining Volumes.—Some such simple relationship between the volumes of the reacting gases and of the reaction products, as was pointed out in the case of the union of hydrogen and chlorine, is found in all reactions in which gaseous substances only are involved. Thus one or two or three volumes of one gas always react with one or two or three volumes of some other gas. Also the ratio of the total volume of reacting substances to the total volume of reaction products can always be expressed as a ratio of small whole numbers. These facts have been called **Gay-Lussac's Law of combining volumes** in memory of Gay-Lussac, who first observed them. This law is one of the strongest supports of Avogadro's law and of the molecular theory. According to the latter, only whole molecules can react with one another and only whole molecules can result from the reaction. Thus N molecules of one substance can react only with N or $2N$ or $3N$, etc., molecules of some other substance, and N or some integral multiple of N molecules must result. N molecules of the first substance occupy the same space as N molecules of any other substance and it is, therefore, easy to see why the regularities and simplicity summarized in Gay-Lussac's law should exist.

Formulae of Non-volatile Substances.—For substances which cannot be volatilized readily and must on this account be studied in the solid or the liquid state, there is no simple law stating anything about the number of molecules in a given volume or

weight. Consequently, there is no advantage, as there is for gases or vapors, in basing the calculations on the weight of 22.4 liters. Any convenient weight of the substance may therefore be chosen for the calculations. If the original analytical data are at hand, they may be used. In general, however, the analytical data have been reduced to percentages, and in that case 100 grams of the substance is a convenient quantity with which to start the calculation. For example, ferric oxide contains 30.06 per cent of oxygen and 69.94 per cent of iron. This means that in 100 grams of ferric oxide there are 30.06 grams of oxygen and 69.94 grams of iron. The atomic weights of oxygen and of iron are, respectively, 16 and 55.84. Hence, in 100 grams of ferric oxide, there are 30.06/16 or 1.875 gram atomic weights of oxygen, and 69.94/55.84 or 1.25 gram atomic weights of iron. The result of these calculations might be expressed in the formula $Fe_{1.25}O_{1.875}$. But this formula has nothing to commend it. It certainly does not represent the number of atoms per molecule of ferric oxide and it has not even the advantage of convenience, for it is no easier to remember the subscripts 1.25 and 1.875, than it is to remember the original analytical data from which they were obtained.

The inconvenient subscripts obtained in the preceding paragraph for the formula of ferric oxide, resulted from the use of the weights of the elements contained in 100 grams of the compound. It would, however, have been just as logical to have chosen some other weight for the calculation. Had a smaller one been employed, the number of gram atomic weights obtained would have been smaller also; had a larger weight of compound been used, the number of gram atomic weights of the elements would have been larger. But the ratio of the number of gram atomic weights would have remained the same. It is, therefore, permissible to multiply or to divide the subscripts in the formula, $Fe_{1.25}O_{1.875}$, by any number, provided both subscripts are multiplied or divided by the same number; so doing obviously does not change the ratio of the number of gram atomic weights represented by the subscripts. Dividing both numbers by the smaller of the two converts the smaller into the number 1, and in this case, the larger into 1.875/1.25 = 1.5. The formula

thus obtained is $Fe_1O_{1.5}$. This formula is far simpler than the first, but not yet entirely satisfactory. If the new subscripts are now multiplied by 2, the formula Fe_2O_3 results. This one is easy to remember; moreover it does not imply the existence of fractions of atoms in the molecules.

It must be borne in mind that the multiplications and divisions performed are purely arithmetical steps, carried out to obtain a convenient formula. The subscripts 1.0 and 1.5 might have been multiplied by 4 instead of by 2, or by any other even number, and would have given convenient subscripts as a result of the process. Obviously then, the formulae Fe_4O_6, Fe_6O_9 or, in general, $Fe_{2x}O_{3x}$ are just as correct as the simplest one, Fe_2O_3. At present no method is known for determining in liquid, or especially in solid substances, what is the number of atoms per molecule. It is, therefore, not possible to decide which of the various formulae written above is correct; all that can be said is that in each molecule of ferric oxide there are 2 atoms of iron for every 3 of oxygen. The formula, Fe_2O_3, is used only because it is the simplest; it would be better to write $(Fe_2O_3)_x$ but the subscript x is usually omitted. The situation is the same for all other solid substances and for most liquid ones.[1]

The **method** developed in the preceding paragraph for finding the formula of a non-volatile substance may be summarized as follows: (1) Divide the weight of each element contained in any definite weight of the compound by the corresponding atomic weight in order to obtain the number of gram atomic weights of each element. In general, these numbers are not whole numbers. (2) Divide the number of gram atomic weights of each element by the smallest of them. (3) If as a result of the second step some of the resulting numbers are still not whole numbers, multiply them all by some integer which converts all of them into whole numbers. In almost every instance this

[1] Methods for determining molecular weights of dissolved substances and, therefore, formulae of soluble liquids and solids are described in Chapter X, page 142. In some cases, further applications of the X-ray analysis of crystals may lead to the determination of molecular weights of solids. In other cases, the term molecular weight may prove to be of little significance as applied to solids. (See page 362.)

integer can be found by inspection; if it cannot, one integer after another may be tried until the correct one is discovered. Difficulty in finding the proper integer occurs only when the data are not accurate.

To show how easily the formula of even a fairly complex substance may be calculated by the method described, one other illustration is given. The mineral, serpentine, is composed of 29.71 per cent of magnesium, 23.05 per cent of silicon, 1.64 per cent of hydrogen and 45.60 per cent of oxygen. From these data the weight of each element in 100 grams of the compound may be otained by inspection. Each of these weights is then divided by the atomic weight of the corresponding element, thus giving the number of gram atomic weights of each per 100 grams of the compound, as follows:

for magnesium, 29.71/24.32 = 1.222
for silicon, 23.05/28.3 = 0.8145
for hydrogen, 1.64/ 1.008 = 1.627
for oxygen, 45.6 /16 = 2.85

The provisional formula is, therefore, $Mg_{1.222}Si_{0.8145}H_{1.627}O_{2.85}$. Each subscript is now divided by the smallest, 0.8145, giving the numbers 1.5, 1.0, 1.998, and 3.499 respectively. Obviously, the last two may be called 2.0 and 3.5. Since not all of these numbers are integers, each is multiplied by 2, thus giving the final formula, $Mg_3Si_2H_4O_7$.

Chemical Equations

The preceding discussion of formulae makes the understanding of chemical "equations" [1] a simple matter. Every such equation is a record in compact form of experimentally determined facts. For example, from the equation

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl,$$

[1] The term chemical "equation" is really a misnomer, because the quantities on the two sides of the "equation" are not equal to one another, except in total weight. For this reason the equality sign is not used in this text. It is replaced by an arrow.

one may read the following: 16.032 grams of methane (CH_4) react with 70.92 grams of chlorine (Cl_2) to give ($\rightarrow$) 50.484 grams of methyl chloride (CH_3Cl) plus 36.468 grams of hydrogen chloride. These statements follow from the equation because the formulae of the substances involved in the reaction and the relative weights have been experimentally determined. Furthermore, since all of the substances are gases, this equation states also that the volume occupied by these weights of each is 22.4 liters when reduced to standard conditions.

Two points are called to the student's attention. In the first place the total weight of the reactants, that is of methane and chlorine, is 86.952 grams, which is exactly equal to the total weight of the reaction products, methyl chloride and hydrogen chloride. The law of conservation of matter, that there shall be neither loss nor gain of weight, is therefore obeyed. If this did not follow from the manner in which the equation is written, the equation could not be correct. The same thing may be put in another, perhaps simpler way. The number of gram atomic weights of each element is the same on the two sides of the equation—thus there is 1 gram atomic weight of carbon, represented by 1C, on each side, and similarly there are 4 of hydrogen and 2 of chlorine on each side. In writing equations it is essential to make sure that the law of conservation of mass is not violated. This can be done by adding up either the total weights in grams, or the total number of gram atomic weights on the two sides of the equation. This method of checking the correctness of an equation is called **"balancing."** The fact that an equation is balanced does not necessarily prove that it is correct. Thus the equation: $CH_4 + Cl_2 \rightarrow CH_2Cl_2 + H_2$ is balanced. But the reaction indicated is not the one which actually occurs, and the equation is therefore not correct because it is not a record of experimentally determined facts.

Calculations from Equations.—The second point to be recalled is that the law of definite proportions applies to all reactions. For example, in the reaction between methane and chlorine, 16.032 grams of methane yield 50.484 grams of methyl chloride. According to the law of definite proportions, then:

the yield from 1 gram of methane
$= 50.484/16.032$ grams of methyl chloride,
and
the yield from x grams of methane
$= x \times (50.484/16.032)$ grams of methyl chloride.

Similarly the weight of methane required to produce any desired amount of methyl chloride can be calculated:

1 gram of methyl chloride requires:
$16.032/50.484$ grams of methane
and, therefore
y grams of methyl chloride require:
$y \times (16.032/50.484)$ grams of methane.

In the same way may be calculated the weight of any one of the substances resulting from, reacting with, or required to produce any desired weight of any of the other substances taking part in the reaction. Since all of the reacting substances are gases, the volumes obtained in any given case may also be calculated by the same method. According to the equation, 22.4 liters of methane yield 22.4 liters of hydrogen chloride, measured at 0°, 760 mm., and the same volume of methyl chloride; therefore, 250 c.c. of methane must produce 250 c.c. of each of these gases. Not only is this true at standard conditions; it is correct at any temperature and pressure since the volumes of all gases are altered in the same way by changes in temperature and pressure.[1] Finally, it is possible to calculate the volume of any one of the substances reacting with or obtained from any given weight of one of the others. Thus the equation states that 16.032 grams of methane give 22.4 liters of hydrogen chloride at standard conditions. Therefore, to be specific, 50 grams of methane yield $(22.4/16.032) \times 50$ liters of hydrogen chloride. But this calculation is correct only at standard conditions because the weight of 22.4 liters of methane is 16.032 grams only at 0°, 760 mm. If the volume of the hydrogen chloride obtained were to be measured at 20° and 740 mm., it would be $(22.4/16.032) \times 50 \times (293/273)\ (760/740)$, since rise in temperature and lowering

[1] Except for deviations from the gas laws.

of pressure both increase the volume of a gas. Volume relations, of course, apply to gaseous substances only.

Limitations of Equations.—In the interpretation of the equation under discussion, nothing has been said of the **conditions** under which the reaction proceeds nor of the completeness of the reaction. Chemical equations in general tell nothing about these important considerations—they are records only of relative weights and, if the reacting substances are gases, of relative volumes. For example, the reaction used as an illustration is a very slow one under ordinary conditions. It requires the action of heat or light to make it proceed with sufficient speed to be useful. It is impossible to include the whole story of a chemical experiment in so compact a form as that of an equation. However, in this book we shall in some cases indicate the necessary conditions by writing a word above the arrow as illustrated in the following:

$$CH_4 + Cl_2 \xrightarrow{\text{light}} CH_3Cl + HCl$$

Further Illustrations of the Method of Making Equations.—Since students using this text have already had considerable experience in writing and interpreting equations and in making calculations from them, only one further illustration is necessary. When lead dioxide is heated in a stream of hydrogen, lead and water are formed. Experiment has shown that from 100 grams of lead dioxide 86.62 grams of lead are obtained, if the reaction is allowed to go to completion. The formula of lead dioxide is PbO_2 and its formula weight [1] therefore is 207.2 + 32 or 239.2 grams. If 100 grams of the dioxide give 86.62 grams of lead, 239.2 grams of the dioxide must yield $239.2 \times 86.92/100$ or 207.2 grams of lead. But 207.2 is the atomic weight of lead and is represented by the symbol Pb in the skeleton equation:

$$PbO_2 + \text{Hydrogen} \xrightarrow{\text{heat}} Pb + \text{water}$$

[1] The term, "formula" weight is used for solids and liquids in place of "gram molecular weight" because, as explained on page 71, the molecular weights of substances in these states are not known. The formula weight is the sum of the gram atomic weights of each element multiplied by its subscript in the formula.

In this are written symbols for the substances, the relative weights of which have been determined. Names are given for the others. The formula of hydrogen is known to be H_2 and that of water to be H_2O. There are 2 gram atomic weights of oxygen on the left side of the equation and consequently there must also be 2 gram atomic weights of oxygen on the right. In order to have the correct number of gram atomic weights on the right side, it is necessary to write $2H_2O$, since in no other way can 2 gram atomic weights of oxygen be obtained without using an incorrect formula for water. But the two formula weights of water contain 4 gram atomic weights of hydrogen, and $2H_2$ must be placed on the left side of the equation in order to balance it. The final result is:

$$PbO_2 + 2H_2 \xrightarrow{\text{heat}} Pb + 2H_2O$$

In *interpreting the equation*, it should be noted that the relative weights of all of the substances involved may be read from the equation: 239.2 grams of lead dioxide + 4.032 grams of hydrogen give 207.2 grams of lead + 36.032 grams of water. On the other hand, hydrogen is the only one of the substances which is a gas at ordinary temperatures, and is, therefore, the only one about the **volume** of which the equation gives any information. Thus 2×22.4 liters of hydrogen (H_2) react with 239.2 grams of lead dioxide. Since the reaction proceeds at high temperature, the volume of steam may also be calculated.[1] Thus at 250° C. the volume of steam obtainable from 239.2 grams of lead dioxide is $2 \times 22.4 \times (523/273)$ liters at a pressure of 1 atmosphere.

Because of certain regularities in the number of molecules which react with one another, it is often possible to write equations without knowing the weights of the reacting substances, provided that the reacting substances and their formulae are known with certainty. For example, magnetic iron oxide (Fe_3O_4) reacts with hydrogen to give iron (Fe) and water. These facts may be stated in a preliminary way by writing:

$$H_2 + Fe_3O_4 \rightarrow Fe + H_2O$$

[1] It is assumed that the gas laws apply strictly.

Inspection shows that the equation is not balanced, for there are 3 gram atomic weights of iron and 4 of oxygen in the substances on the left, and but 1 of each on the right. By putting 3Fe and $4H_2O$ on the right, this difficulty is overcome. But there are then 8 gram atomic weights of hydrogen on the right, and only 2 on the left. Hence, another change is necessary; $4H_2$ must be used on the left. The completely balanced equation now reads:

$$4H_2 + Fe_3O_4 \rightarrow 3Fe + 4H_2O$$

But one must always bear in mind that writing equations in this way is nothing but a repetition of the work of the original experimenters, who, by determining the relative weights of the reacting substances, ascertained what substances are involved in the reaction and their formulae. The student must never forget that, to have any value, **an equation must be a record of experiment,** even though the experiments upon which it is based need not necessarily all have been made at the same time or by the person setting up the equation.

EXERCISES

(1) Make a list of all of the facts recorded in the formulae of the following *gaseous* compounds: (*a*) ammonia, NH_3; (*b*) hydrogen chloride, HCl; (*c*) butane, C_4H_{10}.

(2) From the data given in problem (13), page 62, calculate the formulae of each of the gaseous compounds involved. Use 12 for the atomic weight of the element *E* and 1.0 for that of hydrogen. Note that all of the compounds consist of two elements only and that the per cent of the second element, hydrogen, may therefore be readily obtained from the data given.

(3) Make the same calculations required in (2) for each of the compounds involved in problems (14) and (15), page 63. Include the compound mentioned in (14, *c*), which contains only element *D* and chlorine. The first compound of problem (15) contains only element *F* and chlorine, the others only *F* and hydrogen. For the atomic weights of *D* and of *F* use the values found by you in your solution of these problems. For the atomic weights of the other elements in this and in the following problems, take the values from the table of atomic weights.

(4) A gaseous compound, consisting of 52.17 per cent of carbon,

34.78 per cent of oxygen and 13.05 per cent of hydrogen weighs 1.59 grams per liter at 75° C. and 750 mm. (corr.) What is its formula? (*Ans.* C_2H_6O.)

(5) A compound, consisting of 13.60 per cent of hydrogen, 21.60 per cent of oxygen and 64.79 per cent of carbon, is liquid at ordinary temperatures but may readily be volatilized. At 100° C. and 740 mm. pressure, 1 liter of the vapor weighs 2.357 grams. What is the formula of the substance?

(6) What is the experimental evidence that the molecules of hydrogen gas consist of two atoms?

(7) What facts are recorded in the formula of the solid, cane-sugar, $C_{12}H_{22}O_{11}$?

(8) What are the formulae of the solid substances the percentage compositions of which are given below:

I		II		III	
	Per Cent		Per Cent		Per Cent
Chromium	68.41	Oxygen	9.33	Sodium	32.39
Oxygen	31.58	Lead	90.67	Phosphorus	21.85
				Oxygen	45.06
				Hydrogen	0.70

(9) Ten grams of an oxide of mercury yields 9.617 grams of mercury and 0.383 gram of oxygen on complete decomposition. What is its formula?

(10) (*a*) What weight of oxygen is obtained by complete decomposition of 100 grams of mercuric oxide: $2HgO \rightarrow 2Hg + O_2$? (*b*) What volume of oxygen is obtained by the complete decomposition of 75 grams of the same substance if the volume of oxygen is measured at S. C.? (*Ans.* (*a*) 7.38 grams; (*b*) 3.88 liters.)

(11) (*a*) What weight of oxygen is obtained by the complete decomposition of 100 grams of lead dioxide according to the equation:

$$2PbO_2 \rightarrow 2PbO + O_2$$

(*b*) What volume of oxygen, measured at S. C., is obtained by the decomposition of 75 grams of the same substance? (*c*) What weight of lead dioxide would have to be used to furnish 10 grams of oxygen by the reaction given in (*a*)? (*d*) What weight of lead dioxide would have to be used to obtain 5 liters of oxygen measured at S. C.? (*e*) What weight of lead dioxide would have to be used to obtain 5 liters of oxygen if the latter were measured at 20° C. and 750 mm.? (*e*) What would be the

total volume of the gas obtained if the oxygen were collected over water at this temperature and pressure? (The partial pressure of water vapor in contact with liquid water at 20° is 17.4 mm. See page 26.)

(12) The decomposition of 2 liters of ammonia gas at high temperature leads to the formation of 1 liter of gaseous nitrogen and 3 liters of hydrogen. From these facts, deduce the equation for the reaction.

(13) Using the equation obtained in problem (12) calculate the volume of hydrogen measured at S. C. which is obtained by complete decomposition of 100 grams of ammonia.

(14) One hundred grams of iron unite with 30.1 liters of oxygen, measured at 0°, 760 mm., to form a solid oxide. What is the formula of the latter?

CHAPTER VII

OXYGEN

Relative Activity of the Metals.—Reaction Velocity.—Catalysis.—Oxides and Peroxides

The preceding chapters have dealt with the weight relationships in compounds and in chemical reactions, as well as with some of the theoretical and practical deductions made from them. There are, however, many other characteristics of chemical action which must be studied before even an elementary understanding of the problems of chemistry is possible. These other topics are to be presented in the following chapters in connection with a review of the properties of the more common elements, beginning with oxygen.

Preparation of Oxygen.—Oxygen is one of the most abundant of the elements, constituting about 50 per cent of that portion of the earth to which we have access. About one-fifth, by volume, of the air is oxygen; there are about 89 grams of oxygen in every 100 grams of water, and most of the rocky material, which still abounds on the earth and from which the soil was formed by erosion, contains oxygen as a constituent. In spite of this variety of possible sources for the manufacture of oxygen, only two are commonly employed because of their cheapness and of the ease with which oxygen may be obtained from them. When a current of electricity is passed through water, acidified with a little sulfuric acid, oxygen is liberated at the anode, or positive pole, and hydrogen at the cathode, or negative pole. The mechanism of this process will be discussed in Chapter XIV. The method is used when oxygen of fairly high purity is required; for ordinary commercial purposes oxygen is obtained from the air. Since oxygen is a very active element, capable of reacting with a very large number of substances, and nitrogen is inactive, it is

difficult to remove the nitrogen from air by chemical means without at the same time using up the oxygen. The most practical process consists of first liquefying air, and then allowing it to evaporate slowly. Nitrogen boils at -196° C., while oxygen has a boiling point about 13° higher. Consequently the nitrogen volatilizes first, leaving behind a mixture much richer in oxygen than the original. The gas coming from the remaining liquid finally contains about 96 per cent of oxygen. This is compressed into tanks and is sold as oxygen, since it serves practically all purposes for which oxygen is needed.

The method of liquefying air is an interesting illustration of one phase of the kinetic molecular theory. Molecules of most gases attract one another. The lower the temperature and the greater the pressure, the greater becomes the influence of the attractive force. When a compressed gas is expanded, work must be done against this attractive force in pulling the molecules away from one another. If the gas is allowed to expand slowly this work can be done at the expense of the heat of the surroundings, but if the expansion is sudden, heat from the outside cannot be conducted through the walls of the vessel rapidly enough. The heat of the gas itself is thus expended and the gas becomes cooler. This cool gas is then passed over pipes containing a second portion of compressed gas which is thus brought to a lower temperature. Expansion of this second portion of gas causes a further lowering of the temperature. By a series of such operations, the temperature finally falls below the critical temperature of the gas, and compression then causes liquefaction. Of course the machinery whereby these steps are carried out automatically and economically is relatively complex—the principle is all that can be presented here. Neither this method, which is the cheaper one, nor the method of electrolysis of water is sufficiently inexpensive to permit the manufacture of oxygen at a cost which would make possible its use in many processes to which it might be applied. Here is one of many fields in which further research may yield very useful results.

For the production of smaller quantities of oxygen neither of the two methods described is generally used. In the laboratory oxygen is usually made by decomposing some oxygen compound

such as potassium chlorate. Under the influence of heat the latter decomposes according to the equation:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

A most interesting phenomenon is observed in this reaction. Under ordinary conditions the decomposition is very slow unless very high temperatures are employed, but the addition of a very small amount of manganese dioxide accelerates the reaction sufficiently to make it possible to produce oxygen readily at a temperature far below that at which glass softens. By extraction with water the potassium chloride formed in the reaction may be removed from the residue; if this is done the manganese dioxide is found to have undergone no change either in amount or in properties. So far as superficial examination goes, the substance has accelerated the reaction merely by its presence. This phenomenon is not at all uncommon. It is called **catalysis,** and a **substance which increases the rate of a reaction without apparently taking part in it** is called a **catalyst** or **catalytic agent.** Quite a number of illustrations of catalysis will be encountered in later chapters. In the case of the catalytic action of manganese dioxide on the decomposition of potassium chlorate, no adequate explanation has as yet been advanced; in some other instances the mechanism by means of which the catalytic agent acts seems to have been discovered. It is probable that the mechanism is not the same in all cases, and no attempt will be made to present the various theories which are held at the present time.

Other reactions by means of which oxygen is sometimes made are sufficiently described by the following equations:

(1) $2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$

(2) $2KNO_3 \xrightarrow{\text{heat}} 2KNO_2 + O_2$

(3) $2PbO_2 \xrightarrow{\text{heat}} 2PbO + O_2$

(4) $2HgO \xrightarrow{\text{heat}} 2Hg + O_2$

(5) $3MnO_2 \xrightarrow{\text{heat}} Mn_3O_4 + O_2$

Of these only (1) and (2) are ever used practically; (4) is of historical interest because it was the first method of preparing

pure oxygen. There are of course other compounds from which oxygen may be made, but it is unnecessary to mention them.

The Properties of Oxygen.—At standard conditions oxygen is a colorless, odorless gas, 1 liter of which weighs 1.429 grams. Four volumes of the gas at 0°, 760 mm. dissolve in one hundred parts of water. When liquefied it has a bluish color; the liquid boils at −182.5° and freezes at −227°. The critical temperature is about −118°.

Oxygen is capable of combining with most of the elements and of reacting with a large number of compounds. The rusting of iron and the corrosion of many other metals in air, the phenomenon of combustion, the importance of oxygen to all living organisms are familiar facts concerning the chemical properties of this element.

Oxides and Order of Activity of the Metals.—The products of the union of oxygen with other elements are called **oxides.** Oxides of all of the metals are known, but they cannot all be made by direct union of the elements. Thus gold does not unite with oxygen; its oxide is prepared from other gold compounds. There is a great difference in the tendency of the different elements to combine with oxygen, as is manifested by the varying amounts of heat liberated in the course of the reactions, and by the difference in the speed with which they occur. For example potassium reacts with oxygen rapidly at ordinary temperatures, and the amount of heat liberated is sufficient to melt the metal and to set neighboring objects afire. Iron at ordinary temperatures reacts slowly—in fact water (acting as a catalytic agent) must be present in order that the reaction may proceed at all.

It is not always easy to judge of the tendency of a metal to combine with oxygen by merely allowing the two to come into contact, because in many cases the oxide formed acts as a closely adhering coating on the metal and prevents anything more than surface action. Aluminium, a metal that may be shown by indirect methods to be decidedly reactive toward oxygen, can be kept in air or in oxygen at ordinary temperatures for an indefinite period of time without losing its bright metallic lustre or appearing to undergo any change. Probably a coating of oxide is formed as soon as the metal is exposed to air; this coating, although it

acts as a protective layer and prevents further action, seems to be transparent, and, since it is very thin, does not destroy the luster of the metal. Despite these difficulties in determining the relative ease with which the metals interact with oxygen, it is possible to make a fairly reliable comparison. In the following list some of the metals are arranged in decreasing order of their activity toward oxygen. The list is one which should be thoroughly studied as it will later be found of considerable theoretical and practical interest.

TABLE IV

Order of Activity of Metals

(1) The alkali metals (of which sodium and potassium are examples)
(2) Barium, Calcium
(3) Magnesium
(4) Aluminium
(5) Zinc
(6) Iron
(7) Tin
(8) Lead
(9) Copper
(10) Mercury
(11) Silver
(12) Platinum and Gold

Stability of Oxides.—It is interesting to note that the more readily a metal combines with oxygen, the greater, in general, is the stability of the oxide formed. The term stability must not be confused with reactivity—stability refers to the ease with which a substance is decomposed by heat (or some other form of energy), whereas reactivity refers to the ability of the substance to react with other substances. A substance might be both stable and reactive. This point is well illustrated by the oxides. According to the statement made above, sodium oxide ought to be a very stable compound. As a matter of fact even at very high temperatures it shows no signs of decomposition. Nevertheless in certain respects sodium oxide is a very active substance. On the other hand, mercuric oxide is readily decomposed by heat, as is to be expected from the position of mercury in the table, but it is in many ways not a very reactive oxide.[1]

[1] Some writers use the term "stability" in a broader sense. Thus it might be said that sodium oxide is stable toward heat and unstable toward water, and that mercuric oxide is stable toward water but unstable toward

Hydroxides.—The oxides of many of the metals are capable of combining with water to form hydroxides as illustrated by the equations:

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Most of the hydroxides thus formed are bases. A base is a substance which reacts with an acid to form a salt and water; a more satisfactory definition of this term will be given in Chapter XIV. Many of the hydroxides may again be transformed by heat into oxides and water. It is a curious fact that the more readily the oxide is formed by the action of oxygen on the metal, and the more stable the oxide, the more stable also is the hydroxide. Thus sodium hydroxide cannot be decomposed into the oxide and water at any temperatures as yet artificially realized; calcium hydroxide loses water and gives calcium oxide at moderately high temperatures; copper hydroxide loses water at fairly low temperatures (at 100° a part of its water is given off); and the hydroxides of mercury and of silver are so unstable that they cannot be prepared. The table, made to show the relative ease with which the metals unite with oxygen, has thus been found useful in correlating several other facts and will be found of further use.

Oxygen combines also with non-metals, as illustrated by the following reactions:

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$C + O_2 \rightarrow CO_2$$

$$S + O_2 \rightarrow SO_2$$

The oxides of the non-metals like those of the metals, combine with water, but the resulting hydroxides are in general acids and not bases. An acid, for the present, may be defined as a sub-

heat. The usage followed in this book is more specific and simpler. But the term reactivity must not be used in too broad a sense. Thus sodium oxide is more active than mercuric oxide toward water, but the latter is the more active oxidizing agent.

stance capable of reacting with a base to form a salt and water. The formation of acids is illustrated by the equations:

$$P_2O_5 + H_2O \rightarrow 2HPO_3 \text{ (meta-phosphoric acid)}$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (carbonic acid)}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ (sulfurous acid)}$$

These formulae for the three acids may make it appear strange that they were called hydroxides above; the formulae may, however, also be written as follows: PO_2OH, $CO(OH)_2$ and $SO(OH)_2$. The latter method, though not so commonly used as the former, has some advantages as will be made clear in the chapters in which such acids are discussed. It is fully as correct as the former. Acid-forming oxides are called **acid anhydrides.**

The Burning of Solids in Oxygen.—All natural phenomena, even those which at first glance seem very simple, must be subjected to thorough analysis before they can be fully understood. This may be illustrated by the following study of the well-known fact that solids which burn in air, burn with a much more brilliant evolution of light in an atmosphere of oxygen. Since **the amount of light radiated by a hot body is dependent chiefly on its temperature,** substances apparently get hotter when they burn in oxygen than when they burn in air. The analysis of the problem in question therefore resolves itself into an inquiry as to the reasons for this fact.

There are three factors which determine the extent of the rise of temperature, (1) the nature of the substance heated, (2) its quantity, and (3) the amount of heat available for raising the temperature. The first two are important because the amount of heat required to raise the temperature of a given amount of material a given number of degrees is different for different substances, and because the larger the weight of material to be heated the larger the amount of heat must be. Thus it takes a certain amount of heat to raise the temperature of 1 gram of water from 15° to 16°. This amount of heat is taken as a unit and is called a **calorie.** To raise the temperature of the same weight of iron 1° requires approximately only 0.1 of a calorie. The number

of calories needed to produce a rise of 1° in temperature in 1 gram of material is the **specific heat** of that material. This is one of the characteristic constants of every substance.

The next step in the discussion is to apply what has just been learned to the problem to be solved. The problem may be simplified by assuming that in the one case, the solid is burned in a vessel containing enough air for complete combustion and that, in the other case, the solid is being burned in an exactly similar vessel filled with oxygen at the same pressure as that of the air in the first vessel. In the second vessel there is more oxygen than is required for the reaction, but the excess is equal in volume to that of the nitrogen of the air in the first container. Equal volumes of nitrogen and of oxygen do not have exactly the same weight, but the difference is relatively small, and, furthermore, the specific heat of gases is so small compared to that of the solid material heated, that the difference in heat required to raise the temperature of the mixture in the two cases is practically negligible for the purpose of the problem in hand.

Since neither the difference in the quantity of material nor that in the specific heats is a very decided one, the important point in the problem must be that of the heat available for raising the temperature. The first thought is that perhaps more heat is liberated when a substance burns in oxygen than when it burns in air. But actual experiment shows that this idea is incorrect. **The amount of heat liberated in a specific reaction or required to carry it to completion is dependent practically only upon the weight of the substance.** Small differences are brought about by carrying the reaction out at different temperatures, but for the present purpose such minor effects may be disregarded. The amount of substance burned, and consequently the amount of oxygen also, are the same whether the reaction is carried out in air or in pure oxygen; hence the total amount of heat liberated is the same in air as in oxygen.

To make any progress in the solution of the problem it is evidently necessary to search for some factor which must thus far have been neglected. Careful observation of the phenomenon reveals what that factor is. The substance burns much more **rapidly** in oxygen than it does in air. Application of the

kinetic molecular theory explains why this is true. In order for the substance to burn, its molecules must come into contact with molecules of oxygen. The more molecules of the latter there are in a vessel containing the burning solid, the more often do they strike upon its surface. In other words **the velocity of the reaction varies with the concentration** [1] **of the reacting substances.** If the substance burns faster, the heat is liberated more rapidly and less is lost through the walls of the vessel. More heat is thus available for raising the temperature of the burning substance. There is about five times as much oxygen in a given volume of the pure gas as there is in the same volume of air. The speed of the reaction is, therefore very much greater in the former, sufficiently greater in fact, to explain the greater amount of light radiated when a solid burns in oxygen instead of in air.

Endothermic and Exothermic Reactions.—In the preceding, only reactions which liberate heat were discussed. These are **exothermic** reactions. There are many others, however, which absorb heat—for example the decomposition of mercuric sulfide, of ammonia, or of silver oxide. Reactions of this type are **endothermic** reactions. In endothermic as in exothermic reactions, the heat required to carry them to completion is proportional to the weight of the reacting substances.

Relation of Reaction Velocity to Concentration and to Temperature.—In discussing the burning of solids in air and in oxygen, it was shown that the velocity of reaction varies with the concentration of the reacting substances. Reaction velocity is influenced also by the temperature. Rise of temperature increases it in all cases; for most reactions a rise of about 10° doubles or triples the velocity. Unless this fact is taken into consideration, erroneous conclusions may readily be drawn from a superficial study of the effect of heat on reactions. For example, mercury and oxygen apparently do not unite at room temperature. At about 100° reaction takes place slowly, and mercuric oxide is formed. If the temperature is raised much

[1] The concentration is usually expressed in terms of the number of gram molecules per liter. For gases, this is proportional to the partial pressure of the gaseous substances in question.

higher, the mercuric oxide again decomposes into the elements. It might be concluded from these facts that heat first causes union and then decomposition. This is not exactly correct. At ordinary temperatures, the rate of union of the elements is too slow to be observed. Rise of temperature accelerates the reaction so that it occurs in measurable time. If the temperature is raised further, the heat causes decomposition.

Influence of Other Factors on Reaction Velocity.—That other factors besides temperature and concentration affect reaction velocity is evident from the description of the catalytic action of manganese dioxide and other catalytic agents. Still another point to be considered is illustrated by the different behavior of massive and finely divided iron. The former rusts rather slowly in air; but when the metal is in the form of an extremely fine powder it practically catches fire in air, that is, it reacts so rapidly that the minute particles are raised to their glowing temperature before the heat developed by the reaction is lost to the surroundings. (See also page 594.) The fine powder has a much larger surface per unit volume than has the massive metal, and to this difference the greater speed of the former must be ascribed. Intimate contact also promotes chemical action. Thus if sulfur is powdered on a mercury surface, the two substances interact but slowly; but when the two are ground together they unite in a very short time. Obviously the chemical forces at play act only through very small distances. A thin film of air between two solids is sufficient to prevent their interaction. In the same way, a film of oxide so thin that it does not appreciably dull the luster of the metal seems to prevent the oxidation of aluminium under ordinary conditions. In many cases, however such films are porous, and consequently do not protect the metal. Iron, for example, completely disintegrates by rusting because the oxide formed is of loose texture and does not adhere tightly to the metal surface. When the relative surfaces of the reacting substances are very large, these surface effects likewise assume greatly increased importance, as is described in Chapter XXIX.

Self-sustaining Reactions.—The ideas and facts just presented enable one to understand why some substances continue to react

once the reaction has been started by heating the materials, while other reactions need constant application of heat. At ordinary temperatures, for example, a piece of paper does not react appreciably with oxygen of the air. When the paper is heated the speed of reaction is increased and slow combustion sets in. The reaction is exothermic, but when it is going on very slowly the heat is developed more slowly than it is lost to the surroundings. On heating the paper more strongly, the velocity of reaction is further increased, and ultimately becomes so great that heat is generated more rapidly than it is carried away. The paper will thus get hotter and hotter, and heat from an external source need no longer be supplied to keep the reaction going. The temperature at which a substance burns sufficiently rapidly to maintain the reaction is often called the **kindling point.** This obviously is not a definite temperature, since it must depend upon the temperature, character of the surroundings, and other factors. Thus iron, which ordinarily rusts very slowly, is when very finely divided oxidized by air so rapidly that it is heated to glowing.

Spontaneous combustion of certain varieties of soft coal, of oil-soaked waste, and of similar combustible materials is another illustration of the same kind. In these cases the combustion proceeds even at room temperature, continuously generating heat. Consequently, if the heat cannot escape, the temperature rises. The reaction is thus hastened, causing evolution of more heat and further rise of temperature, until ultimately the reaction becomes fast enough to be dangerous. For this reason spontaneous combustion is prevented by what at first seems a strange method—freely exposing the material to air. Of course air does not stop combustion, but free circulation of air about the material prevents it from getting hot.

If a reaction is accompanied by the absorption of heat, it can never become self-sustaining because the reacting substances cannot supply the heat necessary to maintain a temperature high enough for reaction to go on.

Peroxides and Hydrogen Peroxide.—When sodium is burned in oxygen, the product of the reaction is not the simple oxide, Na_2O, but a substance richer in oxygen as shown by the formula

Na_2O_2. It is called sodium peroxide. Similar reactions occur when the other alkali metals (lithium, potassium, rubidium and caesium) and barium, react with oxygen.[1] These peroxides are very reactive substances. They readily give up the oxygen which they contain in excess over that in the simple oxide, to substances which can unite with oxygen—in other words they are excellent **oxidizing agents.** When dissolved in water or treated with dilute acids, they give hydrogen peroxide according to the equations:

$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$$[2]

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

The hydrogen peroxide, thus formed, very readily decomposes, especially in alkaline solution, giving water and oxygen. In the presence of a slight excess of acid, hydrogen peroxide is very much more stable. While hydrogen peroxide is moderately stable in aqueous solution free from alkalies, slight traces of impurities enormously accelerate its decomposition. Small amounts of alkali have this effect, as well as many salts such as those of iron and manganese, some oxides (of which manganese dioxide is an example) and finely divided platinum and other metals. The effect of all of these substances may be classed as catalytic, because there is no apparent consumption of the catalytic agent. The decomposition of the hydrogen peroxide may in all cases be expressed by the equation:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Although hydrogen peroxide is quite extensively used for various purposes, only a few of its reactions can be mentioned here. It is a weak acid; the acid properties account for the existence of the salts called peroxides. It is an oxidizing agent and owes its usefulness as a

[1] The formulae of the peroxides are not all analogous to that of sodium peroxide. Potassium, for example, forms not only K_2O_2, but also K_2O_4 and possibly other compounds.

[2] This equation is not in contradiction to equation (1) page 82, in which the fact that sodium peroxide yields oxygen on treatment with water was recorded. Water and sodium peroxide give hydrogen peroxide which almost immediately decomposes into oxygen and water.

bleach and as a mild disinfectant to this property. It is, curiously, also a reducing agent. The last named properties will receive further discussion when the matter of oxidation and reduction is taken up. The reactions of hydrogen peroxide are illustrated by the following equations:

Oxidizing property:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

$$2KI + H_2O_2 + H_2SO_4 \rightarrow K_2SO_4 + I_2 + 2H_2O$$

Reducing property:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$$

When oxygen reacts in the presence of water or with substances containing hydrogen, hydrogen peroxide is often produced in small quantities. For example, it is found as a product when hydrogen burns. Of course, because of the high temperature resulting from this reaction, the hydrogen peroxide is usually decomposed at once and can be obtained only when the reaction is carried out under conditions which protect the peroxide from decomposition. Several theories about the way in which oxygen reacts have been based on these facts.

It must be borne in mind that there are many "higher" oxides which are not peroxides although they were at one time erroneously so named. For example, lead forms the two oxides PbO and PbO_2, and manganese several oxides, two of which are MnO and MnO_2. In neither case is the compound which contains the larger *percentage* of oxygen a peroxide because neither reacts with water or with dilute acids to give hydrogen peroxide.

Ozone.—When oxygen flows through a tube through which a silent electrical discharge [1] is passing, the gas issuing from the

[1] The apparatus for preparing ozone may be built as follows: Two pieces of glass tubing are selected, of such diameters that one of them can be slipped inside of the other. The larger tube is coated on its outer surface with tin-foil, and the smaller tube has a similar coating on the inside. The tin-foil is then electrically connected with the terminals of an induction coil. The two tubes are sealed together at the ends, but with inlets and outlets so placed that air can be passed between the two tubes. When the induction coil is put into action a "silent" discharge of electricity occurs from one layer of tin-foil to the other.

tube has properties different from those of ordinary oxygen. It is bluish in color, has a penetrating odor, and is much more reactive than ordinary oxygen. In time these properties disappear. The density of the gas issuing from the apparatus is higher than that of pure oxygen. When the gas is condensed by liquid air and most of the material allowed to evaporate at a very low temperature, there remains behind a blue liquid which, when the temperature is raised, evaporates to form a deep blue gas. 22.4 liters of this gas at standard conditions weigh approximately 48 grams, indicating that the substance responsible for the new properties is a form of oxygen having the formula O_3. This form of oxygen is called **ozone.** Everyone is familiar with its odor—on bright, clear days it is formed in the air by the action of light on oxygen. To it have been ascribed medicinal properties, whether rightly or incorrectly cannot here be discussed.

Ozone is both very reactive and very unstable. It decomposes at ordinary temperatures into oxygen ($2O_3 \rightarrow 3O_2$) with moderate speed; slight rise of temperature greatly hastens the decomposition. It is a powerful "oxidizing" agent; even such inactive metals as mercury are rapidly converted by it into their oxides. Lead sulfide is oxidized to lead sulfate, and many dyes are bleached by ozone. It is on this account readily decomposed by many substances; rubber tubing, for example, rapidly destroys it, and must therefore not be used in the apparatus in which ozone is prepared.

From what has been said, ozone may be looked upon as a modification of oxygen, of different molecular weight and more reactive than the ordinary form of oxygen. Sulfur, carbon, iron, to cite only a few illustrations, also exist each in several modifications, and the same is true of many compounds. But the phenomenon is relatively rare among gaseous substances. Among the latter, active modifications of hydrogen and of nitrogen, which are formed by discharges similar to that by which ozone is ordinarily made, may be given as illustrations. The exact nature of these modifications has not as yet been finally determined and for this reason they will not be described further.

EXERCISES

(1) Give four methods for preparing oxygen. Which of those mentioned are used for the manufacture of the substance on the large scale?

(2) Calculate how much oxygen, measured at S. C., is obtained by complete decomposition of 100 grams of each of the following substances: (*a*) potassium chlorate; (*b*) potassium nitrate; (*c*) lead dioxide; (*d*) mercuric oxide. Judged from this point of view alone, which one of the substances is best suited for use in the preparation of oxygen?

(3) Why do gases cool when they are suddenly expanded?

(4) Describe the method of liquefying air. How is oxygen obtained from liquid air?

(5) (*a*) What is a catalytic agent? (*b*) Why is the function of manganese dioxide in the preparation of oxygen from potassium chlorate classed as "catalytic"?

(6) (*a*) How may the relative activity of the metals be roughly determined? (*b*) In what other respects does the list of metals thus obtained prove to be of importance?

(7) (*a*) Classify the oxides of various elements into two groups. (*b*) What kind of elements form oxides belonging to the one and what kind of elements form oxides belonging to the other group?

(8) What is the specific heat of a substance?

(9) Upon what does the amount of heat liberated in a given chemical reaction depend?

(10) (*a*) What three factors have been shown to determine the velocity of a given chemical reaction? (*b*) Upon what other factor does reaction velocity in general depend? (In answering consider the rate of burning of iron and that of sodium in air of the same temperature and pressure.)

(11) Why do substances burn more rapidly in oxygen than in air?

(12) In view of your answer to (11) explain why the substances are raised to a higher temperature when they burn in oxygen than when they burn in air.

(13) (*a*) What is an endothermic and what an exothermic reaction? (*b*) Which type of substances, those which react endothermally or those which react exothermally with oxygen, may be spontaneously combustible? Why?

(14) Explain why rise of temperature first enables mercury and oxygen to combine and, when continued, causes the oxide formed again to decompose.

(15) Explain the difference between the terms "stability" and "reactivity." Illustrate.

(16) (*a*) How may a peroxide be distinguished from an oxide? (*b*) Which metals form peroxides when they react with oxygen? (*c*) What is the position of these elements in the list which shows the order of activity of the metals?

(17) Describe some of the properties of hydrogen peroxide.

(18) Describe the preparation and properties of ozone. How is its formula determined?

(19) As a review, write the formulae of the following substances: sodium peroxide, ferric oxide, potassium nitrate, lead dioxide, hydrogen peroxide, potassium chlorate, mercuric oxide, phosphorus pentoxide, sulfur dioxide, carbonic acid, calcium oxide, sodium hydroxide.

REFERENCES

Moore—History of Chemistry, Chapters V and VI, will be found very interesting in connection with this chapter of the text.

Alembic Club Reprint—Numbers 7 and 8, Discovery of Oxygen. Priestley (1775); Scheele (1777). Number 3, Cavendish, Experiments on Air.

Rogers—Manual of Industrial Chemistry, 3d. ed., pages 238–242, contains more detailed description of the manufacture and uses of ozone. (In later references will be called "Industrial Chemistry.")

Mellor—Comprehensive Treatise, Vol. I, pages 868–876, describes the liquefaction of gases and the manufacture of oxygen from liquid air.

Cartledge—Inorganic Physical Chemistry, pages 209–212, gives a number of illustrations of catalysis and a brief discussion of some of the simpler theories to account for it.

CHAPTER VIII

HYDROGEN

Reversible Reactions and Equilibrium.—Valence

Hydrogen is a constituent of water, of animal and vegetable tissues, of foodstuffs, of almost all "organic" compounds and of all acids; the element itself is employed in laboratory reactions and in industrial operations. Despite its importance, it constitutes only about **one per cent** of the mass of the earth's crust. But the number of atoms represented by this weight is large compared to the number of atoms of most of the other elements, because hydrogen has the smallest atomic weight of all elements.

Preparation of Hydrogen.—The method most commonly used in the laboratory for the preparation of hydrogen is the **action of certain metals on dilute acids** such as hydrochloric or sulfuric acid. If the speed of the reactions is determined under strictly comparable conditions, such as equal character and area of the surface exposed, equal temperature, concentration and so on, great differences are found. Potassium and sodium react so rapidly and so much heat is developed that the hydrogen may catch fire, and serious explosions may result. Calcium and barium react more slowly, but still too rapidly for convenient handling. When magnesium and aluminium are used, the reaction proceeds very quickly; manganese, zinc, iron and nickel, in the order named, react more slowly, while tin and lead act extremely slowly. Copper, bismuth, antimony, mercury, silver, platinum and gold do not react with acids to give hydrogen. Because of the relative cheapness of zinc and iron, they alone need be considered for practical purposes.

Those metals which, like the first four named, react most easily with acids, **react also with cold water** to give hydrogen and the hydroxide of the metal. The order of their activity toward

water is the same as toward acids. Those next in the list are less active toward water. For instance magnesium reacts with boiling water (if the surface of the metal is kept free from oxide), and iron with steam at red heat to give hydrogen and the oxide of the metal. Tin and lead act only very slowly with steam even at very high temperatures; metals which do not react with acids do not react with water in any condition.

The relative activities of the metals towards acids and water are the same as their relative activities towards oxygen. When it is further recalled that this is also the order of the stability of the oxides and hydroxides of the metals, it is readily understood that the list must represent some progressive change in an important property of the atoms of these elements. This property will be described in a later chapter when more facts are at hand.

The equations which represent the reactions described above for obtaining hydrogen are as follows:

$$2K + 2H_2O \rightarrow 2KOH + H_2 \quad (1)$$

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2 \quad (2)$$

The equation for the reaction of sodium with water is similar to (1), that of barium with water similar to (2).

$$Mg + H_2O \rightarrow MgO + H_2 \quad (3)$$

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad (4)$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \quad (5)$$

The equation for the reaction of zinc is similar to (3).

$$2K + 2HCl \rightarrow 2KCl + H_2 \quad (6)$$

$$Ca + 2HCl \rightarrow CaCl_2 + H_2 \quad (7)$$

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2 \quad (8)$$

$$2K + H_2SO_4 \rightarrow K_2SO_4 + H_2 \quad (9)$$

$$Ca + H_2SO_4 \rightarrow CaSO_4 + H_2 \quad (10)$$

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2 \quad (11)$$

The equations for the reactions of the other metals of the list with hydrochloric acid are like equation (7), and with sulfuric acid like equation (10).

Other Methods of Preparing Hydrogen.—Some elements react with bases to give hydrogen as is illustrated by the following equations:

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$
$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$$
$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

These methods are used only under special circumstances which need not be discussed here. For the manufacture of hydrogen on the commercial scale several processes are employed. The most important of these are the reaction of water and iron, already mentioned, the action of steam on coal (carbon) with the subsequent removal of the carbon monoxide simultaneously produced (see page 415) and the electrolysis of water.

Physical Properties of Hydrogen.—The critical temperature of hydrogen is $-241°$, its boiling point $-252°$ and its freezing point $-259°$. These data show that the cohesive forces between hydrogen molecules must be very small, and the gas exceedingly difficult to liquefy. It is very slightly soluble in most liquid solvents. Some metals in the solid condition, for example palladium, are capable of dissolving large volumes of hydrogen. This property partly accounts for the ability of hydrogen to permeate thin sheets of metals. If the hydrogen is confined in a vessel made of one of these metals, it dissolves at the inner surface, diffuses through the metal, and escapes from the outer surface. On account of its low molecular weight, hydrogen has a high rate of diffusion, and readily escapes through porous materials, even though every precaution is taken to make the pores as minute as possible. This is a problem of great importance in the manufacture of the gas bags for balloons and dirigibles in which hydrogen is used because of its buoyancy.

Chemical Properties of Hydrogen.—The chemical properties of hydrogen may be reviewed briefly as follows:

(1) Hydrogen unites with most of the non-metallic elements forming such compounds as hydrogen sulfide, ammonia, methane,

hydrogen chloride, water, etc. In most cases these compounds are more conveniently prepared by indirect methods, since hydrogen either does not react at all with non-metals at ordinary temperatures, or acts very slowly, and many of the compounds are decomposed at temperatures high enough for rapid reaction. Even the union of hydrogen and oxygen, which at 700° proceeds explosively, is slow at temperatures as high as 500°. This reaction may, however, like many other reactions in which hydrogen is involved, be greatly accelerated by **catalytic agents**; finely divided metals here play an important rôle.

(2) Hydrogen reacts with some metals to form hydrides, of which NaH and CaH_2 are examples. In contrast to the oxides which are generally quite stable, all of the hydrides of the metals are unstable. The formation of the hydrides and the ease with which they again decompose may account in part for the apparent solubility of hydrogen in metals, and for the catalytic action which metals display in reactions involving hydrogen.

(3) Hydrogen combines with certain classes of compounds. On account of the property of being able to unite with hydrogen (and with some other substances) such compounds are called **unsaturated.** The hardening of liquid fats by hydrogen (in the presence of catalytic agents) is an illustration of this type of reaction.[1]

(4) Hydrogen, at more or less elevated temperatures, acts as a "reducing agent." The term "reduction" was originally applied to a reaction in which oxygen is removed from a compound, for example:

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

Now the term is used in a broader sense which will be explained more fully later. Hydrogen is capable of reducing many oxides. Here again the order of activity of the metals is met with, for the more active the metal the less easily is its oxide reduced.

Reversible Reactions and Equilibrium.—The reaction between hydrogen and the magnetic oxide of iron, which was cited in the

[1] See for example "Creative Chemistry," Edwin E. Slosson, The Century Co., 1921, Chapter XI and particularly pages 202–205. See also page 420 of this text.

preceding paragraph, is of interest theoretically because it is the reverse of the reaction by means of which hydrogen is frequently prepared. When the oxide is to be reduced by hydrogen, an excess of the latter is used, and this excess of the gas carries away the water as fast as it is formed. When the reverse reaction is carried out, an excess of steam is employed, and this carries away the hydrogen as fast as formed. Under these conditions obviously only one or the other of these " opposing " reactions can go on.

Suppose, however, that a certain amount of hydrogen is **placed in a closed vessel** with the oxide. The steam then resulting from the interaction cannot escape, and begins to react with the iron simultaneously produced. At first there is a relatively high concentration of hydrogen, and its reaction with the oxide is relatively fast; at the same time there can be only a little steam present, and according to the principles developed in the preceding chapter, its reaction with the iron must be very slow. As the reaction proceeds, the amount of hydrogen decreases, and its rate of reaction is therefore diminished; at the same time the amount of steam in the confined space increases, and its rate of reaction becomes greater. Ultimately the two reactions must attain the same speed, and when this condition is reached each product will be generated as fast as it is used up. Although both reactions are then still going on, there is no apparent change in concentration of any of the reacting substances and therefore no visible evidence of interaction. Such a condition is called a state of **chemical equilibrium.** Reversibility of reactions is a very common phenomenon of chemistry—in fact some chemists assume that all reactions are reversible, but that, owing to enormous differences in the speeds of the opposing reactions, the net result in some cases is apparently complete reaction in one direction even though none of the reaction products is removed. A thorough understanding of this phenomenon is essential for a full appreciation of many chemical phenomena, and the subject will receive more detailed treatment in Chapter XII.

Valence.—The equations on page 97 for the reactions of various metals with water or with acids show that different amounts of hydrogen are produced by 1 gram atomic weight of

the different metals. One gram atomic weight of sodium liberates 1 gram atomic weight of hydrogen; 1 gram atomic weight of calcium liberates 2; and 1 gram atomic weight of aluminium 3 gram atomic weights of hydrogen. A similar phenomenon is noted when hydrogen compounds are studied. Thus in hydrogen chloride there is 1 gram atomic weight of hydrogen for each gram atomic weight of chlorine, in water 2 of hydrogen for 1 of oxygen, in ammonia 3 of hydrogen for 1 of nitrogen, and in methane 4 of hydrogen for 1 of carbon. Different elements seem therefore to possess different capacities for uniting with or for displacing hydrogen. The number which represents this capacity for a given element in a given compound is called its valence.

The following statements define more sharply the facts just described. (1) **An element, 1 gram atomic weight of which reacts with or displaces 1 gram atomic weight of hydrogen, is said to have a valence of 1, or to be univalent in the compound or the reaction in question.** (2) **The valence of an element in a given reaction or compound represents the number of gram atomic weights of hydrogen, or some other univalent element, with which 1 gram atomic weight of the element in question unites or which it displaces.** Thus, 1 gram atomic weight of potassium displaces 1 gram atomic weight of hydrogen; potassium therefore has a valence of 1. The same conclusion is reached by a study of the reaction of potassium with chlorine. Chlorine, as defined above, is univalent, and 1 gram atomic weight of chlorine combines with 1 of potassium. It is necessary to present the definition of valence from both points of view given because not all elements displace hydrogen or combine with it. The terms univalent, bivalent, trivalent, quadrivalent, quinquivalent are used to designate elements whose valence is 1, 2, 3, 4 or 5, respectively.[1]

When two elements of the same valence unite with or displace each other, they do so in the ratio of 1 gram atomic weight of each. If the valences are not the same, the two elements unite or react in such proportions that the product of the number

[1] The term divalent is sometimes used in preference to bivalent, tervalent in place of trivalent and tetra instead of quadrivalent.

of gram atomic weights of one of the elements by its valence is equal to the product of the number of gram atomic weights of the other element by its valence. This rule is used also in determining the valence of an element in a compound, if the formula of the compound is known. Thus the formula of ferric oxide is Fe_2O_3. The valence of oxygen is 2; the product of valence and number of gram atomic weights is 2×3 or 6. Since there are 2 gram atomic weights of iron, and since this number multiplied by the valence must also be 6, the valence of the iron is 3. The valence of an element is not, however, the same number in all of its compounds or reactions. There are, for example, two chlorides of iron—ferrous chloride, $FeCl_2$, and ferric chloride, $FeCl_3$.[1] In the former, the valence of iron is 2, in the latter 3. The case of manganese is notable; it forms the oxides MnO, Mn_2O_3, MnO_2, MnO_3 and Mn_2O_7.

It must not be concluded from the variability of valence that valence represents merely a formal relationship. The conditions under which an element, which acts in different compounds with different valences, exhibits the one or the other valence are fairly definite.[2] Nevertheless the fact that elements show different valences in different compounds and in different reactions usually makes it necessary to specify to which compound or reaction a certain valence has reference. The following elements, how-

[1] The ending "ous" is used for the compound in which the element of variable valence exhibits the lower valence, and the ending "ic" for the compound in which the higher valence is shown. When more than two valences are exhibited the terminology is, of course, more complex. Thus in manga*nous* chloride, the valence of manganese is 2, in manga*nic* compounds its valence is 3, in manga*nites* the valence is 4, in manga*nates* the valence is 6 and in *per*manga*nates* it is 7. The italicized portions of the words used, show how the various valences are indicated. The endings "ite" and "ate" also indicate that oxygen is a constituent of the compound. Thus FeS is ferrous sul*fide*, $FeSO_3$ ferrous sul*fite*, and $FeSO_4$ ferrous sulf*ate*.

[2] When ferrous chloride is converted into ferric chloride, the iron is oxidized. Changes in valence of an element are always due to processes involving oxidation and reduction. When no such processes occur in a reaction, it is certain that no element involved has undergone valence change. This consideration is often helpful in determining the valence of an element in a compound. These matters and the interpretation of valence are taken up in later chapters, e.g., pages 220, 358.

ever, always exhibit the same valence: the alkali metals (i.e., sodium, potassium, etc.), silver and hydrogen 1, the alkaline earths (i.e., magnesium, calcium, barium, etc.) and oxygen [1] 2, aluminium 3. The constancy of the valence of these elements is of great value in determining the valence of other elements in compounds. Thus 1 gram atomic weight of sodium displaces 1 gram atomic weight of copper from cuprous compounds, but 2 gram atomic weights of sodium are required to displace the same quantity of copper from cupric compounds. Since sodium is always univalent, copper must be univalent in cuprous and bivalent in cupric compounds. Chlorine is univalent in compounds which contain only chlorine and a metal, and this is true of bromine, iodine and fluorine in analogous compounds.

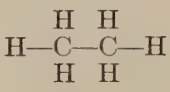
The concept of valence may be extended to groups of elements which react as a unit. Thus the combination of elements, SO_4, known as the sulfate group,[2] is found in many compounds, and the 5 atoms which it contains remain combined with each other in most reactions in which the group takes part. The formula weight of the group, 96 grams, is always found combined with 1 gram atomic weight of bivalent elements, such as barium or calcium, or with 2 gram atomic weights of univalent elements, such as sodium or hydrogen. The sulfate group, therefore, has a constant valence of 2. Similarly the nitrate group (NO_3) is always univalent, the carbonate group (CO_3) always bivalent, the ortho-phosphate group (PO_4) always trivalent. These groups are thus also of value in determining the valence of elements.

Occasionally the strict application of the rule of valence, given above, leads to conclusions which are erroneous. Magnetic oxide of iron has the formula Fe_3O_4. The valence of oxygen is 2; hence, application of the rule leads to a valence of $2\frac{2}{3}$ for that of iron. The difficulty in this and in all similar cases, is that there are two kinds of " iron " in the compound—2 atoms of ferric and 1 of ferrous iron. In other words, the compound is formed by union of a compound in which iron has a valence of 3 with one

[1] In a very few compounds of oxygen, the latter exhibits a valence of 4.

[2] The groups mentioned in this paragraph are all ions. See Chapters XIII and XIV.

in which the valence of iron is 2. Another type of case is illustrated by the substance ethane, C_2H_6. The application of the rule leads here to a valence of 3 for carbon, which, as the word valence is ordinarily interpreted, is incorrect. This discrepancy may be explained by picturing the arrangement of the atoms in the compound in the following manner:



Each atom of carbon is attached to 3 atoms of hydrogen and to 1 other atom of carbon, or to what might be considered as the univalent (CH_3) group. Formulae such as the one just given are called "structural" formulae and are described more fully in Chapter XXVIII.

Since information about the valence most frequently exhibited by the more common elements greatly simplifies remembering formulae of their compounds, the data given in this chapter together with a few additional ones are summarized in the following Table V. The table refers only to the valences exhibited by the elements in compounds containing but 2 elements or 1 element and a radical. A few of the common radicals have also been listed in the table. Further discussion of valence is found on pages 195 and 260 and Chapters XVIII and XXIV, in which the questions of the valences of the elements within the radicals, of positive and negative valence, of the relation of valence change to oxidation and reduction, and of the interpretation of the phenomena of valence are taken up. For detailed information about all of the valences of any given element, particularly of those not included in Table V, the chapter dealing with the element in question should be consulted. This table of valence is presented at this point for ready reference, particularly for those unfamiliar with the usual valences of the common elements. The logical way to study and remember valences is in connection with the periodic system. (See Chapter XXII.)

TABLE V

USUAL VALENCES OF SOME OF THE COMMON ELEMENTS AND RADICALS IN COMPOUNDS CONTAINING ONLY TWO ELEMENTS OR ONE ELEMENT AND A RADICAL.

UNIVALENT	BIVALENT	TRIVALENT	QUADRIVALENT
hydrogen *	magnesium *	boron	carbon
sodium *	calcium *	aluminium *	silicon
potassium *	strontium *	antimony	
lithium *	barium *	bismuth	
silver *	zinc *	arsenic	
	cadmium		
	nickel		
	cobalt		
	lead		
copper in cuprous compounds	copper in cupric compounds	chromium in chromic compounds	
mercury in mercurous compounds	mercury in mercuric compounds		
	iron in ferrous compounds	iron in ferric compounds	
fluorine *	manganese in manganous compounds	manganese in manganic compounds	
chlorine			
bromine			
iodine	tin in stannous compounds		tin in stannic compounds
nitrate (NO_3)*	oxygen	(nitrogen in ammonia)	
acetate ($C_2H_3O_2$)*	sulfur in sulfides		
chlorate (ClO_3)*			
permanganate (MnO_4)			
	sulfate (SO_4)*	phosphate (PO_4)*	
	carbonate (CO_3)*		
	chromate (CrO_4)*		
	dichromate (Cr_2O_7)*		
	oxalate (C_2O_4)*		

Elements or radicals marked * always exhibit the valences listed in this table. Those not so marked exhibit other valences in some of their compounds. For details see the chapters dealing with these elements.

EXERCISES

(1) Mention all of the properties of the metals and their compounds which follow the order of activity given in the list on page 84.

(2) Give four methods for preparing hydrogen, and for each write the equation of a reaction illustrative of the method.

(3) What is the evidence that the molecules of hydrogen gas exert but little attraction on each other?

(4) Name four properties of hydrogen gas. Should you say that hydrogen at ordinary temperatures is a very reactive substance? Give reasons for your answer.

(5) What is a reversible reaction? Illustrate.

(6) (*a*) Explain why the reaction between iron and steam goes to completion when the latter is passed over hot iron. (*b*) Explain why the reaction between hydrogen and the magnetic oxide of iron (Fe_3O_4) goes to completion when hydrogen is passed over the oxide. (*c*) What occurs when the oxide of iron and hydrogen are heated together in a closed vessel?

(7) Describe what is meant by chemical equilibrium.

(8) (*a*) How many gram atomic weights of hydrogen are displaced by the action of hydrochloric acid on 1 gram atomic weight of each of the following metals: sodium, aluminium, barium, zinc, lead, calcium, potassium, tin, magnesium? (Assume that an excess of hydrochloric acid is present.) (*b*) What may one conclude from these facts with regard to the valence of each of these metals? (*c*) What weight of hydrogen chloride is decomposed in each of the reactions?

(9) What is the valence of each element or group in the following compounds (groups are indicated by parentheses): PbO, HBr, Na(OH), $(NH_4)Cl$, $K(MnO_4)$, $K_2(SO_4)$, $Ce(SO_4)_2$, $Ca(SO_4)$, $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Ba(ClO_3)_2$? (The answers may be indicated by placing small Roman numerals above each element or group in the formula of each compound.)

(10) Assuming the valences of the elements or groups to be those found in problem 9, write the formula of each of the following compounds: calcium permanganate, ammonium sulfate, calcium chloride, lead sulfate.

REFERENCES

ROGERS—Manual of Industrial Chemistry, 3d. ed., pages 538–540, describes briefly the manufacture of gases consisting chiefly of hydrogen for use in balloons. In the same volume, pages 701–710, is a description of the hydrogenation of oils.

CHAPTER IX

WATER AND THE PROPERTIES OF LIQUIDS

Vapor Tension.—Boiling and Freezing Points.—Hydrates and Similar Compounds

The properties of water and its importance to life and industry are too well known to require further detailed description. Because it is so extensively used in chemical processes as a nearly inert solvent, its chemical activity is often overlooked. Attention is therefore again called to its reactions with metals and with oxides; its ability to react with salts and with other classes of compounds will be taken up later. In this chapter, certain phenomena characteristic of all substances are to be studied, and water will be used merely as an illustration.

Equilibrium between Vapor and Liquid.—It has repeatedly been pointed out that molecules of gases attract one another. If the temperature is sufficiently high and the containing volume sufficiently large, the molecules move so rapidly and at such distances from each other that these attractive forces do not greatly affect the behavior of the gas. But as the velocity of the molecules is decreased by cooling the gas, and as they are brought more closely together by compression, the influence of the attractive forces becomes more and more noticeable. Ultimately this effect becomes so great that the molecules can no longer freely move away from or past each other, and the gas condenses to a liquid.

In spite of the attractive forces, the molecules of a liquid are still in motion. But the molecules do not all move at the same rate—some of them have a much higher and others a much lower speed than the average value.[1] The point at which a gas must liquefy, as a result of cooling and compression, is the point

[1] See page 22.

at which the molecules are so close to each other and are moving so slowly that those moving at the **average** velocity are held together. The molecules with a velocity greater than the average can therefore still escape from the body of the liquid. Since, at any given temperature, there is a definite proportion of molecules having the excess velocity necessary to overcome the attractive forces, the number of molecules which escape from unit area of liquid surface in unit time must also be fixed at this temperature.

The phenomenon just described from the kinetic molecular view point is called **evaporation.** Since the more rapidly moving molecules escape, the average velocity of the molecules left behind during evaporation must decrease. This means that the temperature of the liquid must fall.[1] In order that evaporation may go on unchecked, the liquid must absorb heat from its surroundings and thus exert a cooling effect.[2] Practical use is frequently made of this phenomenon. Porous earthenware absorbs water freely and distributes it over a fairly large surface. From this evaporation is rapid, and is accompanied by a decided cooling effect. The water containers of the ancients, who lived in warm climates, were constructed on this principle, and the so-called iceless refrigerators of modern times differ from the old devices only in improvements brought about by more scientific selection of the porous materials. Some liquids evaporate more rapidly than others, and therefore exert a greater cooling influence. This explains the use of a substance like ethyl chloride in local anaesthesia. When it is sprayed upon the skin, it evaporates so rapidly that it freezes the tissues, and makes them temporarily insensitive to pain.

When evaporation takes place from an open vessel, the molecules of the liquid escape into the air, and most of them diffuse away. Occasionally one of them may strike an air molecule and rebound into the liquid, but this is a relatively rare occurrence, and if heat is continuously supplied all of the liquid evaporates. Suppose, however, that the liquid is in a closed vessel which it does not completely fill, and that the space above

[1] See page 22.

[2] The cooling is due also in part to the fact that work is done by the escaping molecules against the attraction exerted by the others.

the surface of liquid is a vacuum. The molecules which escape from the surface pass into this empty space, and travel onward until they strike a wall of the vessel. There they rebound, ultimately to penetrate again into the body of the liquid. Since evaporation is by no means instantaneous, there are relatively few molecules in the space above the liquid immediately after the latter has been introduced into the vessel. Consequently only a few molecules rebound back into the liquid. Under these conditions more molecules leave the liquid than return to it. The number of molecules in the vapor therefore increases; more of them rebound into the liquid until, finally, the numbers leaving the liquid and returning to it become equal. When this condition has been reached there is no longer any change in the relative number of molecules in the vapor and in the liquid, although evaporation and condensation are still taking place. This then is a state of equilibrium such as has already been described for a chemical reaction, but since only one variety of molecule is involved, it may be called a state of **physical equilibrium.**[1]

Any change in the system which alters the relative number of molecules leaving and entering the liquid must of course destroy temporarily this state of equilibrium. Thus the vessel in question may be a cylinder and piston, and its size may be enlarged by drawing the piston further out. The molecules in the vapor or gas [2] must consequently travel farther before they strike the wall of the vessel and return to the liquid. The number returning in unit time is then smaller than it was before the piston was drawn out. Consequently, more molecules escape from the liquid into the vapor than return to the liquid; this condition brings about an increase in the number of molecules in the vapor, until finally a new condition of equilibrium is set up. During

[1] In this case, as in so many others, hard and fast distinctions between chemical and physical changes should not be made. Attractive forces between molecules are akin to chemical forces, and evaporation, which involves these forces, is a process not entirely different from a chemical process.

[2] There is no essential difference between a vapor and a gas. Gases which can readily be condensed by lowering of temperature are commonly called vapors.

these changes, nothing has been done to alter the number of molecules which leave the surface of the liquid; the number of molecules which strike this surface from above must therefore be the same in the newly set up state of equilibrium as in the original one. In Chapter II it was shown that, at a given temperature, the number of molecules of a gas or vapor which strike unit surface of any enclosing wall of a vessel is proportional to the pressure. Enlarging the space above the liquid, although it changes the number of molecules in that space at equilibrium evidently does not change the pressure, since the number of molecules striking unit surface is unchanged. This pressure, which the vapor of the liquid exerts when vapor and liquid are in equilibrium, is called the **vapor tension of the liquid.**[1]

The same sort of reasoning shows that decreasing the space above a liquid, which has reached equilibrium with its vapor, results in the condensation of some of the latter without, however, causing a change in the pressure of the vapor. **The vapor tension of a liquid, therefore, has a constant value at a given temperature.** Different liquids, even though they may be at the same temperature, have different vapor tensions. For example, ether and ethyl chloride, which at room temperature evaporate much more rapidly than water, have much greater vapor tensions than water, and mercury, which evaporates very slowly, has a much lower vapor tension.

[1] Difficulty is sometimes encountered in understanding the difference in the terms "vapor pressure" and "vapor tension." A vapor exerts a pressure just like any other gas, whether liquid is present or not. Ordinary air contains water vapor, and this vapor has a partial pressure the value of which depends upon the amount of water in the air. Usually the air is not saturated with water vapor. This simply means that if the air is placed in contact with liquid water, more of the latter evaporates and the partial pressure of the water vapor, i.e., its vapor pressure, increases. Ultimately, however, the air becomes saturated. In other words, the increase in the amount of water vapor in the air ceases, the partial pressure of the water vapor no longer grows larger—a condition of equilibrium has been set up. This maximum vapor pressure is clearly the same pressure as that called the vapor tension. The vapor tension is then the limiting value of the vapor pressure, which the latter approaches as complete saturation of the space in contact with liquid is approached.

The Effect of Change in Temperature on Vapor Tension.— Rise of temperature of a substance means an increase in the average velocity of its molecules. The higher the temperature of a liquid, the larger must be the number of molecules with a velocity sufficient to enable them to escape from the restraint of the attractive forces. Raising the temperature of the liquid, therefore, increases the number of molecules which leave its surface in unit time. In order to maintain the condition of equilibrium between vapor and liquid, established before heat is applied, it is necessary to increase also the number of molecules entering the liquid from the vapor, and this can be done only by increasing the pressure of the latter. The increase may be brought about simply by fixing the volume of the vessel and allowing the liquid to evaporate until the required pressure is attained, or by applying more pressure to the vapor by means, for example, of a piston. The method of increasing the pressure is not important; the significant conclusion is that **rise of temperature raises the vapor tension of the liquid.**

It is a matter of considerable interest to know the value of the vapor tensions of common liquids, particularly of water, at various temperatures. An illustration of the usefulness of this information has already been given in Chapter II. Since vapor tensions are expressed in terms of the pressure of the vapor at equilibrium, any units used to express the pressures of gases or of vapors may be used for vapor tensions. The most common unit is, of course, millimeters of mercury. A table of the vapor tension of water at various temperatures is given in Table VI.

A more convenient method of tabulating such values for certain purposes is the graphical one shown in Fig. 4. Here distances to the right of the vertical reference line represent temperatures, while distances above the horizontal reference line represent vapor tensions in millimeters of mercury.[1] The values of these distances in terms of temperature and of vapor tension are shown in the figure. As a matter of interest the values of the vapor tensions of several different liquids at various temperatures are shown on the same diagram. The various points, representing

[1] In the customary terminology, temperatures are plotted as abscissae and vapor tensions as ordinates.

TABLE VI

VAPOR TENSIONS OF WATER

TEMPERATURES C°.	VAPOR TENSION MM. OF MERCURY	TEMPERATURES C°.	VAPOR TENSION MM. OF MERCURY
0	4.6	27	26.7
1	4.9	28	28.3
2	5.3	29	30.0
3	5.7	30	31.8
4	6.1	35	42.1
5	6.5	40	55.3
6	7.0	45	71.9
7	7.5	50	92.5
8	8.0	55	118.0
9	8.6	60	149.4
10	9.2	65	187.5
11	9.8	70	233.7
12	10.5	75	289.1
13	11.2	80	355.1
14	12.0	85	433.6
15	12.8	90	525.8
16	13.6	95	633.9
17	14.5	96	657.6
18	15.5	97	682.1
19	16.5	98	707.3
20	17.5	99	733.2
21	18.65	100	760.0
22	19.8	125	2,347.4
23	21.1	150	3,570.7
24	22.4	175	6,695
25	23.8	200	11,661
26	25.2		

the vapor tensions and temperatures for each liquid, are connected by lines. The drawing of such lines has the advantage of joining points which represent data for the same substance, and of making it possible to estimate the value of the vapor tension at some temperature lying between any two temperatures for which the data have actually been determined. All of the curves are quite similar, although they are not identical in curvature and

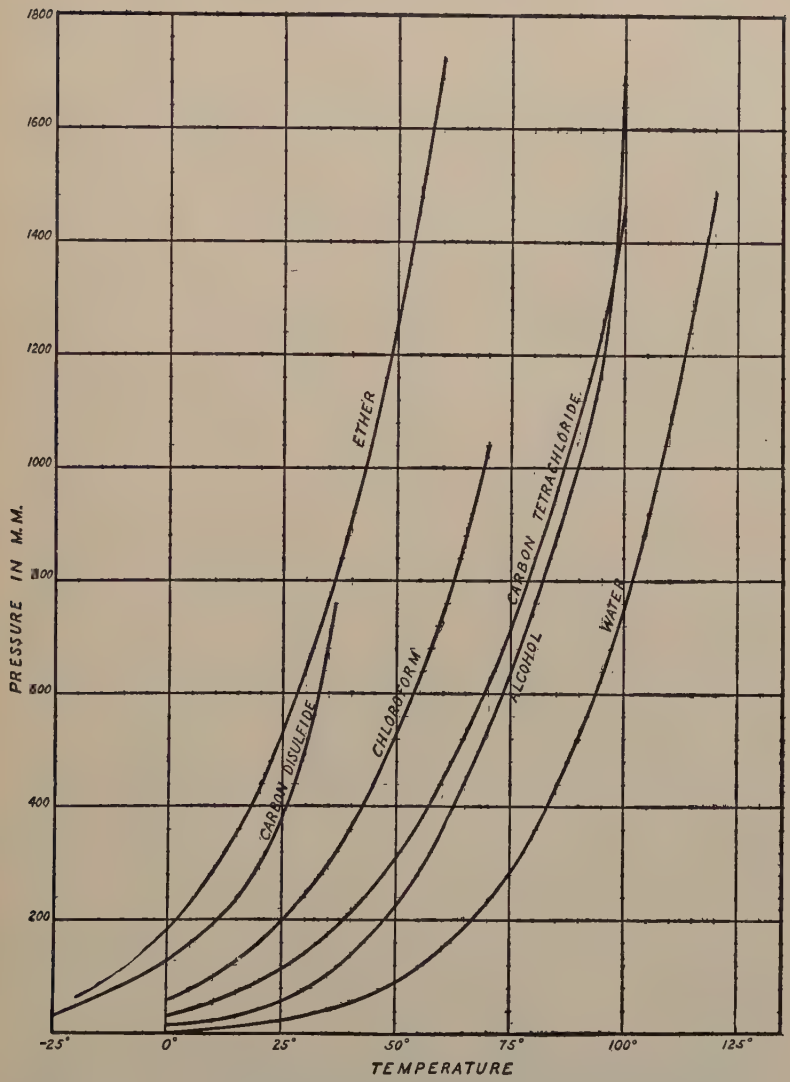


FIG. 4. — VAPOR TENSIONS (IN MM. OF MERCURY) FOR SEVERAL LIQUIDS AT VARIOUS TEMPERATURES (IN °C).

lie in different parts of the diagram. This is consistent with the difference in the vapor tensions of the substances represented.

Boiling Points.—When a liquid is allowed to evaporate into the open air instead of into a vacuum, the pressure which the vapor exerts constitutes only a part of the total pressure. As the temperature of the liquid is raised, the vapor tension rises, but, since the vessel containing the liquid is an open one, the total pressure must remain the same. Hence, the molecules of the liquid substance must be displacing those of the air. Ultimately the temperature becomes so high that the vapor tension becomes equal to the total external pressure. Further application of heat can therefore no longer produce an increase in the pressure, and the temperature of the liquid must remain constant. Under these conditions, the heat merely increases the speed of evaporation—that is it increases the speed with which the velocity of the slower molecules is brought to the value at which they can escape. If heat is supplied fast enough, more molecules acquire the critical velocity than can escape from the surface of the liquid. Vapor must therefore form as bubbles within the body of the liquid and the familiar phenomenon of boiling results. Since the vapor of which the bubbles consist has the same pressure as that of the surroundings, the bubbles will neither be crushed nor will they burst by expanding as they rise to the surface.[1] The **boiling point of a liquid is,** therefore, **the temperature at which the vapor tension of the liquid becomes equal to the pressure of the surrounding atmosphere.** Since atmospheric pressure varies, the boiling point also must vary; from the curves of Fig. 4, the boiling points at different pressures can be determined for the liquids for which data are given. Commonly, boiling points are recorded for an external pressure of 760 mm.; these temperatures are called the "normal boiling points."

Distillation.—The phenomenon of evaporation may be put to practical use when two substances, one of which is much more volatile than the other, are to be separated. When such a mixture is heated the more volatile substance evaporates first,

[1] The slight difference in pressure between the top and the bottom of the boiling liquid is neglected in the discussion.

and the other remains behind. The volatile material may be recovered if the apparatus, in which the heating is carried out, is so designed that the vapor can be condensed by cooling after it has been removed from the residual liquid. The process of evaporating and recondensing a liquid is called **distillation.** From what was said in the preceding section, it is evidently desirable to carry out the evaporation of the liquid at its boiling point, for at this temperature evaporation proceeds at the maximum speed. This statement does not necessarily mean at the normal boiling point; distillation is often carried out in a partial vacuum in which the boiling point may be considerably lower than at atmospheric pressure. Many liquids decompose before the temperature is reached at which their vapor tensions become 760 mm.; for the distillation of such liquids "**vacuum distillation**" must be resorted to. In other cases vacuum distillation is employed because it may effect a better separation of the mixture into its components, or because it proves more economical to use power in creating the necessary vacuum than in raising the temperature of the liquid.

Heat of Evaporation.—During the processes of evaporation, heat must be supplied to the liquid in order to maintain the average kinetic energy of the molecules. The amount of energy required when 1 gram of liquid is evaporated is called the **heat of vaporization.** This quantity varies somewhat with the temperature; most commonly it is stated for the temperature of the normal boiling point. For the conversion of 1 gram of water at 100° into steam 540 calories are required and, conversely, when 1 gram of steam condenses to water at 100° the same amount of heat is set free.

Vapor Tension of Solids. Melting and Freezing Points.—Every one has probably observed that solids evaporate, but that the rate of evaporation is smaller than that of the same substance in the liquid state. On clear sunny days in winter, for example, although the temperature may be considerably below 0° C., evaporation very quickly diminishes the amount of snow. Solid iodine gives off a violet vapor far below its melting point. Evaporation of both solids and liquids is explained in identical fashion. Because of the lower temperature, evaporation from

a solid surface is slower than from the surface of a liquid. With rise in temperature the vapor tension of solids increases and, as has been shown by experiment, the rate of increase is greater than in the case of the corresponding liquid. Consequently the vapor tension of the solid must ultimately become equal to the vapor tension of the liquid as is illustrated in Fig. 5. Above this temperature, the solid has the higher vapor tension, and, if solid and liquid are contained in the same closed vessel, the space above the liquid contains more vapor than corresponds to equilibrium. Some of the vapor must therefore condense into the liquid. Below this temperature, the liquid has the higher vapor tension, and vapor must condense upon the solid. Only at the temperature at which the vapor tension of the solid is equal to that of the liquid can the two exist side by side. This temperature is, therefore, the freezing, or melting point of the substance. As was described in the first discussion of the phenomenon of freezing (pages 36–37), solidification of a substance is caused by the influence of the attractive forces. When the substance melts, this influence must be overcome by supplying energy—the quantity of heat required to melt 1 gram of substance is called the **heat of fusion.** To melt 1 gram of ice, 79 calories are required—the same amount of heat is given off when 1 gram of water freezes.

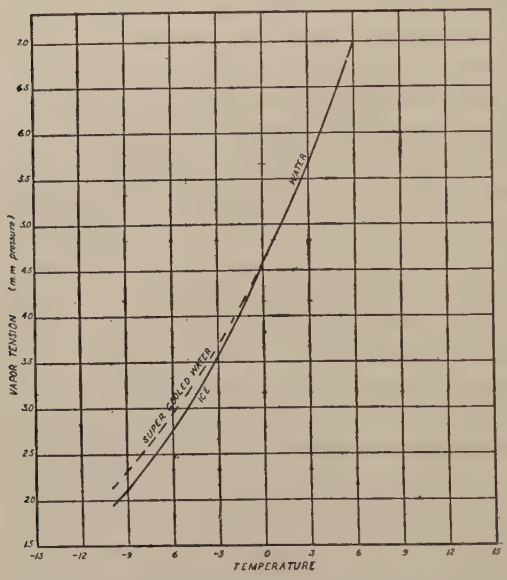


FIG. 5. — VAPOR TENSIONS OF ICE AND OF WATER AT VARIOUS TEMPERATURES.

Super-cooling.—It will be noticed that in Fig. 5, data are given for the vapor tension of water at temperatures below 0° C., the freezing point. These could be obtained because it is possible to cool water, and other liquids, below their freezing points without causing the change to the solid form. This phenomenon is called **super-cooling.** Super-cooling often causes trouble when an attempt is made to freeze a liquid. Methods of preventing it are to introduce into the liquid at its freezing point, or slightly below, a small crystal of the solid, or to scratch the inside of the vessel with the sharp point of a glass rod.

Just why these procedures are effective in preventing super-cooling is not fully understood. A possible explanation may be as follows. In order that a crystal may form, the molecules of the substance must come together in some specific, orderly fashion. This occurs relatively rarely by chance alone. If a crystal of the solid is present, its faces, edges and corners attract the molecules of the substance more or less strongly because the number of molecules in the different portions of the crystal surface is different. The crystal may therefore act as a directive force to gather the molecules in the necessary orderly arrangement. A scratch on the inside of the vessel may act in a similar fashion, because at its irregular surface there may be inequalities in the number of molecules, causing directed attraction of the molecules of the liquid. Since, in scratching the sides of the vessel, many hundreds of scratches of all shapes are made, there may be a few of the right shape to start crystal growth. These explanations are not thoroughly adequate because they do not account for the differences in the ease with which different liquids can be made to crystallize nor to the differences in the degree of super-cooling possible.

Hydrates.—Water often combines with other compounds to form new compounds which are called hydrates. Thus 1 molecule of sodium carbonate unites with 10 of water to form the decahydrate of sodium carbonate. Its formula is written $Na_2CO_3 \cdot 10H_2O$ (rather than $Na_2H_{20}CO_{13}$) to indicate that sodium carbonate and water are not firmly united in the compound, and that the latter readily breaks up again into the components from which it was made. The ordinary concepts of

valence do not account for the reaction between these two substances, and the manner in which the atoms are joined in such complex compounds [1] is not yet fully understood. For this reason also, it is good practice to use for them a method of formulation which is different from that used for simpler compounds.

Since hydrates are compounds of definite composition, their properties should be different from those of the parent substances. This difference may readily be observed in the physical properties. Hydrates differ in melting point, density, solubility, often in color, and so on from the original compounds from which they were made. Thus copper sulfate is white while the hydrate, $CuSO_4 \cdot 5H_2O$, blue vitriol, is dark blue; cobalt chloride is deep-blue, but the hydrate, $CoCl_2 \cdot 6H_2O$, is red; chromic chloride is deep violet and insoluble in water, whereas its hydrates have entirely different colors (see below) and are very soluble. The difference in the chemical properties is not always so obvious because hydrates are often so unstable that they completely dissociate under the conditions of the chemical tests applied. This happens, for example, when an attempt is made to find differences in chemical behavior between sodium carbonate and its decahydrate in reactions occurring at high temperatures. On the other hand, it is impossible to detect any differences in reactions between the two substances when the reactions are carried out in aqueous solution. Perhaps this is because, under this condition, the sodium carbonate exists only in hydrated form. Very little is known in most cases about the existence of hydrates in solution, and since the reactions

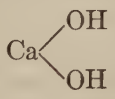
[1] The term " complex compounds " used to be reserved for compounds of greater stability than that of most hydrates, but formed like the hydrates by the union of two or more molecules of different kinds. There seems to be no good reason for making the distinction. Hydrates were formerly also called " compounds with water of crystallization," and this term is still frequently employed. The origin of this name lies in the fact that the hydrates are generally obtained when a compound, capable of hydrate formation, is crystallized from aqueous solution. Although there is a possibility that in some instances hydrate formation is related to the process of crystal formation, this is certainly not true in all instances, and the term " water of crystallization " is therefore misleading. It will not be used in this text.

of most hydrates are similar to those of the anhydrous compound (as the non-aqueous component of a hydrate is called), it is customary to omit the water in the formula when writing equations for reactions in which hydrates take part.

This frequent similarity in the behavior of the anhydrous compound and that of the hydrate must not lead to the belief that the latter are not true compounds. The similarity is due, as already explained, to the ease with which most hydrates decompose into the anhydrous compound and water. There are, however, a large number of cases in which the hydrate is fairly stable and, when that is true, marked chemical differences between the anhydrous substance and the hydrate are observable. Likewise, when a substance is capable of forming more than one stable hydrate, the several hydrates each possess distinctive chemical properties. Thus to cite but one example, $CrCl_3 \cdot 4H_2O$, a green substance, behaves quite differently from $CrCl_3 \cdot 6H_2O$, which is gray-violet.

There are instances in which doubt might exist about the proper mode of classification of a compound formed by union of water with another substance—that is, whether to call the resulting substance a hydrate or a simple compound. Thus 1 molecule of calcium oxide unites with 1 molecule of water to form calcium hydroxide. Its formula is written $Ca(OH)_2$ and not $CaO \cdot H_2O$. This is done in spite of the fact that at moderately high temperatures the compound decomposes into the oxide and water. The same thing is true of most hydroxides, and of many other compounds. For example H_2SO_3, sulfurous acid, and H_2CO_3, carbonic acid, are formed by union of water with SO_2 and with CO_2 respectively, and the reverse reaction takes place spontaneously under most conditions. Nevertheless these compounds are not classed as hydrates, for two reasons. Each of these compounds reacts as if it consists of two parts. In the case of calcium hydroxide the two parts are the calcium and the hydroxide, for sulfurous acid they are the hydrogen and the sulfite group, SO_3, and for carbonic acid, the hydrogen and the carbonate group, CO_3. In none of these cases is water one of the characteristic groups which determines the chemical behavior of the substance, as it is in the compounds called hydrates. The

other reason for not calling the compounds just mentioned, and many others like them, hydrates is that the atoms in them seem to be bound in ways that can be explained by the ordinary valences of the elements involved, as illustrated by the formula



But it is by no means certain that there is a fundamental difference between the two kinds of compounds—too little is known about the nature of hydrates to decide this question.

The ability to form **complex compounds** is not limited to water. Ammonia behaves much like water in this respect. For example, the two hydrates of chromium chloride, $CrCl_3 \cdot 4H_2O$ and $CrCl_3 \cdot 6H_2O$, have their exact counterparts in the two compounds $CrCl_3 \cdot 4NH_3$ and $CrCl_3 \cdot 6NH_3$, whose properties differ in much the same way as do those of the corresponding hydrates. Alcohol and many other substances possess the property of forming complex compounds. In fact the property is a very general one for which chemical theory has as yet failed to find an adequate explanation. Many instances of complex formation will be encountered.

Conditions Determining the Formation and the Decomposition of Hydrates.—Since hydrates are often relatively unstable they are formed only under very definite conditions. What these are may be readily understood by the same reasoning used in the study of the mechanism of evaporation. At a given temperature, a given number of hydrate molecules in a mass of the hydrate may be considered to decompose in a given time interval. The resulting water molecules escape from the body of the material in the form of vapor. If the number of water molecules in the surrounding atmosphere is so large that the number returning to the surface of the material is the same as the number escaping, a condition of equilibrium is established in which hydrate is not formed or decomposed in measurable quantities. Evidently this apparent cessation of reaction is due to the equal rate of decomposition and formation of hydrate. Another way of stating this fact is to say that **hydrates have definite aqueous tensions** at definite temperatures; that the hydrate decomposes

and the anhydrous substance does not combine with water when the pressure of the water vapor in the surrounding atmosphere is less than the aqueous tension of the hydrate; that, when the vapor pressure of the water in the surrounding atmosphere is greater than the aqueous tension of the hydrate, the latter does not decompose, but the anhydrous substance unites with water to form the hydrate. A hydrate which loses its water in air of ordinary moisture content is said to be **efflorescent.**

Another factor which determines the stability of hydrates is the temperature. In general, hydrates become more unstable as the temperature rises. This means that increase in temperature is generally accompanied by an increase in the aqueous tension of the hydrate. These relationships will be discussed more in detail in the chapter on chemical equilibrium.

From the preceding discussion it should be clear that when a substance is capable of forming more than one hydrate, the temperature and the pressure of the water vapor in the space surrounding the anhydrous substance determine which hydrate is formed, since each hydrate has its own definite aqueous tension. What has been said of the formation and decomposition of hydrates, is true likewise of all complex compounds which have as one component a volatile substance such as ammonia or alcohol. For such compounds the term "aqueous tension" is of course not used; the more general expression, "decomposition pressure" is employed.

It may be pointed out here that the decomposition of any compound, complex or simple, when one of the products of decomposition is volatile, is influenced by the vapor pressure of the volatile component just as the decomposition of hydrates is influenced by the vapor pressure of water. This is illustrated by the case of calcium carbonate. At any sufficiently high temperature, calcium carbonate decomposes into calcium oxide (quick lime) and carbon dioxide only when the pressure of carbon dioxide in the surrounding air is less than the decomposition pressure of the carbonate.

EXERCISES

(1) (*a*) Why do only relatively few of the molecules of a liquid at temperatures considerably below the boiling point escape from the liquid into the vapor? (*b*) Why does a liquid cool off on evaporation?

(2) (*a*) What happens to the molecules which escape from the surface of a liquid contained in a closed vessel? (*b*) Describe how equilibrium

between a liquid and its vapor is established after the former is placed in an empty vessel.

(3) (*a*) Upon what does the number of molecules of vapor which strike the surface of a liquid depend? (*b*) Define the term "vapor tension." (*c*) What is the maximum vapor tension which a liquid can have, assuming that the liquid is heated in a closed vessel? (In answering (*c*) consider the discussion on page 36.)

(4) Suppose that a liquid and its vapor have come to equilibrium in a closed vessel. (*a*) What would occur if the vessel were opened and air blown through it? (*b*) What would happen to the temperature of the liquid?

(5) (*a*) What is meant by the term "boiling point"? (*b*) What is meant by the "normal boiling point"? (*c*) From the curves of Fig. 4, determine approximately the boiling points at 760 mm. of each of the liquids for which data are given. (*d*) Do the same for the boiling points at 350 mm.

(6) Explain why the vapor tension of a liquid increases with rise in temperature.

(7) Bearing in mind that the freezing point of a liquid is that temperature at which solid and liquid substance may exist side by side, explain why the vapor tension of the solid and of the liquid must be equal at the freezing point.

(8) Why is heat required to melt a solid?

(9) What is the evidence that hydrates are compounds rather than mixtures?

(10) Why is the substance formed by action of water on calcium oxide called calcium hydroxide, $Ca(OH)_2$, rather than a hydrate of calcium oxide the formula of which might be written $CaO \cdot H_2O$?

(11) Suppose that a hydrate has an aqueous tension of 7 mm. What would happen to the hydrate if it were placed in a vessel in which the pressure of water vapor is: (*a*) 4 mm., (*b*) 10 mm., (*c*) 7 mm.? What would happen to the anhydrous substance?

(12) Suggest two methods for causing a hydrate to lose its water.

REFERENCES

FINDLAY—The Phase Rule, 5th ed., pages 65–74, describes the conditions under which hydrates and similar complex compounds are stable.

MELLOR—Comprehensive Treatise, Vol. I, pages 498–504, gives a simpler treatment of the same subject, but the discussion is limited to hydrates. The summary of the properties of hydrates on page 504 is excellent.

CHAPTER X

SOLUTIONS

NATURE OF THE PROCESS OF SOLUTION.—PROPERTIES OF SOLUTIONS.—EQUIVALENT WEIGHTS.—NORMAL AND MOLAR SOLUTIONS.—METHODS OF DETERMINING MOLECULAR WEIGHTS OF SOLUTES

SOLUTIONS play a most important rôle in chemistry. Many reactions, which proceed too slowly to be noticeable or useful when the reacting substances are directly mixed, proceed rapidly if the substances are dissolved and then mixed. This is particularly true of solids. Solids usually cannot be brought into very intimate contact with each other because, no matter how finely they are ground, each solid retains its own crystalline form, and the surfaces of the individual crystals serve as boundaries which interfere with chemical action.

Solutions may be Defined as Homogeneous Mixtures.—When sand mixed with water is allowed to stand, the sand soon separates from the water and settles to the bottom. Such a mixture is clearly not homogeneous—the fact of settling indicates that there are physically distinct portions in the mixture, and observation with the naked eye is sufficient to demonstrate this fact at once. If fine clay is mixed with water the process of settling is extremely slow, and the particles of clay may be so small that they cannot be distinguished without the use of a microscope. Nevertheless, it is readily possible, by using a microscope or by observing the mixture for a long time to demonstrate that it is not homogeneous. There are mixtures of water and of suspended material, so fine that settling in the ordinary sense of the word never occurs. In them the suspended particles do not become visible even under the best microscope. In these cases an instrument called the "ultramicroscope" has been used to demonstrate the presence

of the suspended particles, and these mixtures are therefore not true solutions although they simulate solutions in many respects. There are therefore all gradations between coarse, **rapidly settling, easily filterable,** clearly **non-homogeneous** suspensions or emulsions [1] and **non-settling, non-filterable** solutions which are **homogeneous** under every test which can be applied.[2] Between the two extremes there is a border zone of mixtures in which the suspended particles are so fine that their identification as mechanical entities is extremely difficult. Such mixtures display some of the properties of ordinary suspensions and some of the properties of true solutions. They are called colloidal suspensions and will be discussed separately.

Since solutions have been defined as homogeneous mixtures and since no limitations have been placed on the original physical state of any of the components, it follows that the term is not restricted to mixtures, one component of which is a liquid, although solutions of this sort are the most common and most thoroughly investigated. Since all gases are completely miscible in each other, any mixture of gases might be called a solution. As is well known, solids, liquids or gases can dissolve in, that is form homogeneous mixtures with, liquids. But solids can also dissolve in other solids. If molten gold and molten platinum are mixed, and the mixture is allowed to solidify by cooling, the resulting mass consists of crystals, each of which contains a definite amount of gold and a definite amount of platinum. In these crystals the two substances are distributed in perfectly homogeneous fashion, and each crystal therefore constitutes what is called a solid solution. Such solutions possess all of the properties of liquid solutions except for differences caused by the rigidity of the solid state and the peculiarities of crystalline form. Solutions of liquids or of gases in solids are theoretically possible

[1] An emulsion is a suspension of one liquid in another. Emulsions usually do not separate into their components by settling as readily as do suspensions. This is due to the fact that liquids usually do not differ from each other in density as much as do solids from liquids. This, however, is no fundamental distinction.

[2] The term filterable is here used to indicate that the components of the mixture can be separated from one another by filtration.

and seem to have been prepared in a few cases, but such solutions are as yet of no practical importance.

The most striking fact about solutions is that the ability to form these homogeneous mixtures is not an indiscriminate property. Salt is readily soluble in water but not at all soluble in ether, butter fat is readily soluble in ether but not in water, and silica is not appreciably soluble in any known solvent.[1] The definition of solutions as homogeneous mixtures implies that the process of forming a solution is purely physical, whereas the specificity of the relationship between the components able to form solutions implies a chemical relationship. As a matter of fact, solubility is a borderline phenomenon, and argument concerning its classification as a physical or a chemical process is futile.

Diffusion in Solution.—Before attempting to explain why certain solvents dissolve only certain substances, the characteristic properties of solutions must be examined somewhat more closely. No matter how dilute the solution, the **solute,** i.e., the dissolved substance, is uniformly distributed through the mixture. Since solutions may be almost infinitely dilute, this must mean that the material of the solute has been torn apart into its individual molecules. If for example, a minute amount of sugar is placed in the bottom of a beaker and carefully covered with a considerable amount of water, the sugar dissolves, and after a while is found in equal amounts in all portions of the liquid. The sugar molecules in the solid state are held together by attractive forces, but when the sugar dissolves these forces seem to become inactive. Hence the dissolved sugar behaves somewhat like a gas for it "uniformly and homogeneously occupies the space made available to it"[2] and is capable of diffusing through the water. These are properties characteristic

[1] Silica may be "dissolved" in molten sodium hydroxide or carbonate, but in the course of the process the silica is converted into sodium silicate, and the silica cannot be reprecipitated by simply removing the medium in which it appears to dissolve. It is therefore not strictly correct to speak of dissolving the silica, although, as a matter of convenience, chemists often use the term in such cases.

[2] See page 14.

of all dissolved substances.[1] Diffusion of a dissolved substance through a solution is much slower than that of one gas through another, but that difference is due merely to the fact that the diffusing substance encounters many more molecules in a solution than it does in a gas. In the same way gases diffuse much more rapidly into a vacuum than they do into another gas.

An Hypothesis of Solubility.—There are two facts which help to explain the limited ability of substances to act as solvents for other substances. The first is that all gases are completely miscible in each other, and the second, that dissolved substances behave in certain respects like substances in the gaseous state. When a solid dissolves in a liquid, the molecules of the former are apparently pulled far enough apart to destroy the effect of the attractive forces. They are thus allowed to behave somewhat like molecules of a gas. This can occur if the molecules of the solvent attract the molecules of solute approximately as strongly as the molecules of solute attract each other. Under these circumstances the latter are drawn into all parts of the solvent as strongly as toward each other. Since the kinetic energy of these molecules is equal to that of any other molecules at the same temperature, they will diffuse in all directions within the solution as soon as the effect of the attractive forces between them is counterbalanced by the attractive forces exerted by the surrounding solvent molecules.

The ability of the molecules of the solvent to attract those of the solute may be shown not to be the only important factor in bringing about the formation of a solution. If it were, gaseous substances, whose molecules do not need to be "pulled apart" because they do not exert a great effect on each other, should be soluble in all substances. As a matter of fact, gases are,

[1] The process of diffusion may be illustrated if the dissolved material is a colored compound like copper nitrate. This is placed in the bottom of a tall cylinder, which is then carefully filled with water in such a way as to avoid stirring. The best way to carry out the experiment is to fill the cylinder with water, and then to introduce a concentrated solution of copper nitrate into the bottom of the cylinder by means of a long pipette. The greater density of the solution prevents it from becoming mixed with the water by stirring, provided it is introduced slowly. In a few days diffusion will be distinctly noticeable.

in general, but slightly soluble in liquids or solids. To account for this fact, the question must be examined from another point of view. The molecules of a liquid or a solid attract one another strongly. This attraction might tend to squeeze foreign molecules out of the mass of material, somewhat as grease is squeezed from two metal surfaces that are forced close together. But if the molecules of the solvent attract the molecules of the foreign material just as strongly as they do each other, there will be no tendency to " squeeze " the foreign molecules out. This is practically the same as saying that in such a case the solvent molecules are separated from one another by the molecules of solute. Since the molecules of gases do not possess appreciable attraction for each other, they are not likely in general to attract molecules of other substances, and are, therefore, slightly soluble in non-gaseous substances.

The **conclusion** to be drawn from the preceding discussion is that when molecules of A attract those of B with a force whose magnitude is of the same order as that with which A molecules attract each other and as that with which B molecules attract each other, the two substances, A and B, are soluble in each other. If these magnitudes are very nearly the same, the two substances are miscible in all proportions, like alcohol and water, and it is impossible to designate one of them as the solvent and the other as the solute. When the similarity is not so great, the miscibility is limited, either because an excess of one kind of molecules is required to pull the other variety apart, or because of the tendency of the one kind of molecules to " squeeze " the other kind out.

In order to verify and use these conclusions, it would be necessary to have accurate data on the values of these various attractive forces for an enormous number of substances. This information is not at hand nor easy to obtain. It is therefore desirable to relate the attractive forces to some other properties. This can be done only in a very general way, because not enough data have as yet been collected, but some results of general value can be reached. Since the attractive forces between molecules are unquestionably related to the chemical forces which result in compound formation, it is to be expected that chemically

similar substances should have similar attractive forces between their molecules, and should therefore be soluble in one another—a fact which has been known for a long time. There remains, however, the important question of deciding exactly what is meant by the statement that two substances are chemically alike. This is very difficult to do and chemists have by no means solved the problem completely—the latter part of this book is devoted largely to bringing out such similarities and differences. At present only a few illustrations of the principle developed above can be given.

Carbon forms a large number of compounds with hydrogen called hydrocarbons. Since they all contain the same elements, great chemical similarity between them might be expected. These compounds are often soluble in each other. All of them belong to a large class, which for reasons to be given in Chapter XXIV, are called non-polar substances. Salts, acids and bases, on the other hand, belong to a class of substances called polar. In general, polar compounds are more likely to be soluble in other polar compounds than in non-polar ones, and *vice versa*. Thus molten salts are usually, though not always, soluble in each other. Water, which is also a polar substance, is a good solvent for many salts, acids and bases, but not for non-polar compounds like the hydrocarbons. Of course, there are substances whose characteristics are partly those of polar and partly those of non-polar substances, and such substances are somewhat soluble in either of the extreme groups. Thus alcohol is completely miscible with both water and ether, altho gh ether and water are very slightly soluble in each other. It is clear that a more detailed discussion must be deferred until a very much larger number of substances has been studied.

According to the hypothesis outlined, the forces which determine solubility are similar to chemical forces. Hence, it is reasonable to assume that in many instances the formation of a solution is accompanied by the formation of compounds, a large proportion of which are so unstable that they cannot be isolated by ordinary chemical methods. This similarity between the factors responsible for solubility and those responsible for compound formation is shown by the fact that many substances which

are very soluble in water, crystallize from the solution in the form of hydrates. It is not necessary to assume that actual chemical union into aggregates of definite composition must always occur when a solution is formed, although this assumption is made by some chemists.

It must not be forgotten that the preceding explanation of the phenomenon of solubility is still an hypothesis and that many facts must be gathered before it may be considered established. It is useful in giving a mechanical picture of the process, and it seems to agree, as far as is known, with many facts. There are, however, many data which it does not explain. Thus cupric chloride and cuprous chloride (CuCl) might be expected to be chemically somewhat similar, since both are salts of the same elements. Yet the former is very soluble in water while the latter is very insoluble. Again the hypothesis does not explain why barium sulfate is very insoluble in water while magnesium sulfate, which is in many respects very similar to barium sulfate, is soluble. At present there is no theory to account for such differences; the hypothesis which has been discussed in the preceding paragraphs is not only as good as any other, but is elastic enough to fit the facts as they become better known.

Concentration of Solutions.—A number of terms are so frequently used in connection with solutions that a review of their meaning is desirable. The terms solvent and solute have already been employed in this text, and their meaning made clear. When a large quantity of solute is dissolved in unit quantity of solvent, the resulting solution is **concentrated**; when the amount of solute is small, the solution is **dilute.** It is evident that these two terms are not exact; what may be a large amount of solute for one purpose may be a small amount for some other purpose. The exact amount of dissolved material is given by the **concentration** of the solution. This is expressed in a variety of ways. The weight of solute contained in a given weight of solvent is often used. When this method of recording the concentration is employed the value may be expressed in percentages; thus, a 5 per cent sugar solution contains 5 grams of sugar in 95 grams of solvent. More commonly the weight of a solute dissolved in 100 grams of solvent is given.

Very frequently the concentration is stated in terms of molar solutions. A **molar solution** contains 1 gram molecular weight of solute in 1 liter of solution, a 2 molar solution 2 gram molecular weights, a $\frac{1}{10}$ molar solution $\frac{1}{10}$ of a gram molecular weight. For example, a molar solution of sulfuric acid contains 98.076 grams of the acid in 1 liter of the solution; a molar solution of sodium hydroxide contains 40.008 grams of the base per liter. Since the reaction between sulfuric acid and sodium hydroxide takes place according to the equation:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

98.076 grams of the acid react with 2×40.008 grams of the base, and 1 liter of the molar solution of the acid reacts with exactly 2 liters of the molar solution of the base. Had the solutions been made to contain equal weights of acid and base, the volumes of the two necessary for complete interaction would have borne no simple ratio to each other.

There is, however, a disadvantage in the use of molar solutions. Had the base in question been barium hydroxide and had the solution contained 1 gram molecule of the base, 1 volume of the acid solution would have required only 1 volume of the solution of the base (instead of 2 as in the preceding illustration) because the reaction equation for the second case is:

$$H_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2H_2O$$

This difficulty may be avoided if the solutions are made up so as to contain 1 gram equivalent weight per liter instead of 1 gram molecular weight as is described below.

The **equivalent weight of a substance** is that weight (1) which displaces 1 gram atomic weight of a univalent element, or (2) from which 1 gram atomic weight of such an element may be displaced or, in general, that weight (3) which reacts with an equivalent weight of some other substance, in any given reaction. Several illustrations may be cited. In the reaction between hydrochloric acid and the more active metals, 1 gram atomic weight of hydrogen is liberated from 1 gram molecular weight of hydrochloric acid (HCl = 36.468); the gram equivalent weight of the latter is therefore equal to the molec-

ular weight. From 1 gram molecular weight of sulfuric acid (H_2SO_4 = 98.076 grams), 2 gram atomic weights of hydrogen are obtained; in this case the equivalent weight is $\frac{1}{2}$ of 98.076 grams. But from 1 gram atomic weight of phosphoric acid (H_3PO_4 = 98.064 grams), 3 gram atomic weights of hydrogen are obtained, which means that the equivalent weight of this substance is $\frac{1}{3}$ of its molecular weight. Note that in the illustrations thus far cited, the gram equivalent weight is equal to the quotient of the molecular weight by the valence of the element or group of highest valence in the compound. This however, is, not always true. For example, 2 gram molecular weights of potassium permanganate react with hydrochloric acid to liberate 10 gram atomic weights of chlorine according to the equation:

$$2KMnO_4 + 10HCl + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Cl_2 + 8H_2O$$

Hence the equivalent weight of potassium permanganate in this reaction is $\frac{2}{10}$ of its molecular weight. On the other hand, the permanganate reacts with silver nitrate according to the equation:

$$KMnO_4 + AgNO_3 \rightarrow AgMnO_4 + KNO_3$$

The equivalent weight of silver nitrate is equal to its molecular weight since 1 gram atomic weight of silver may be deposited from the latter. According to the third statement of the definition given above, the equivalent weight of the permanganate in the second reaction is, therefore, equal to its molecular weight.

From the foregoing discussion it is evident that substances may have different equivalent weights for different reactions, and that the reaction equation must be known in order to determine the equivalent weight for any given case. However, in most double decompositions, the equivalent weight of each substance is equal to the quotient of its molecular weight divided by the valence of the element or group of highest valence in the compound, as was found for the acids mentioned above.

A solution which contains 1 gram equivalent weight of the solute in 1 liter of solution is called a **normal solution**; one containing 2 gram equivalent weights in this volume is a 2-normal solution and so on. From what was said about equivalent weights it follows that a normal solution of hydrochloric acid

contained 36.468 grams of hydrogen chloride, one of sulfuric acid, $\frac{1}{2}$ of 98.076 grams; a normal solution of potassium permanganate used to liberate chlorine must contain $\frac{2}{10}$ of a gram molecular weight of the permanganate per liter.

The great advantage of normal solutions is that solutions of a given normality always react with exactly equal volumes of any solution of the same normality. Thus 1 liter of a normal solution of sodium hydroxide, barium hydroxide, or any other base will neutralize 1 liter of a normal solution of hydrochloric, sulfuric, or any other acid. This fact is used in determining the strength of solutions of acids or of bases. If, for example, 150 c.c. of a normal solution of sodium hydroxide is required to neutralize 100 c.c. of a solution of sulfuric acid, the latter must be stronger than normal because 100 c.c. of the solution has the neutralizing capacity of 150 c.c. of a normal solution. More exactly, the sulfuric acid solution must be $\frac{150}{100}$ times normal and must therefore contain 1.5 times the gram equivalent weight of sulfuric acid per liter. This method of determining the concentration of a solution is, of course, not limited to reactions between a base and acid; the strength of any solution may be found by determining the volume of some solution of known normality with which a known volume of the solution in question reacts.

The concentration of a solution may not always be stated in the terms desired. It is possible to transform such concentrations into the desired terms if the density of the solution is given. Suppose that a solution contains 10 grams of the solute in 100 grams of the solvent, and that the density of the solution is 1.05. The weight of solution per 100 grams of solvent is 110 grams and since the density is 1.05 the volume of 110 grams of solution is $\frac{110}{1.05}$ c.c. This volume contains 10 grams of solute and the weight of solute contained in 1000 c.c. of solution can readily be calculated. This weight divided by the equivalent weight of the solute gives the number of gram equivalents per liter, and hence the normality. The density of very dilute solutions may be considered to be equal to that of the pure solvent. Similar calculations for the reverse transformation can be made when required.

Saturated Solutions. Equilibrium between Solvent and Solute. —When a solid or liquid is placed in contact with a solvent, the mutual attractions of solvent and solute enable molecules of the latter to leave the surface of the solute and mix with the molecules of solvent. At a given temperature and in the presence of a given solvent a definite number of molecules thus enter into solution. As they do so they accumulate in the solvent, where some of them strike other molecules or the walls of the vessel and return to the surface of the solute. Here they may be retained again as a part of the undissolved material. Evidently in this case, just as in the case of evaporation or of the formation and decomposition of a hydrate, a state of equilibrium is reached when the number of solute molecules entering the solution is equal to that returning from the solution to the undissolved material. It is also clear that such a state of equilibrium cannot be established unless undissolved solute and solution are in contact with each other. A solution in equilibrium with an excess of undissolved solute is called a **saturated** solution. Should the solution, after equilibrium has been established, be removed from the excess of solute (e.g., by filtration or decantation) the solution would still be saturated provided no change in the temperature or loss of solvent by evaporation have occurred. But the only way to be certain that a solution is saturated is to keep it in contact with the solute.

Students frequently make the mistake of defining a saturated solution as one which contains as much solute as the solvent can hold. This is incorrect because under certain conditions a solvent, in the absence of an excess of the solute, can retain more of the latter than corresponds to a state of equilibrium. This may occur when a solution is saturated at one temperature, the excess of solute removed, and the remaining solution cooled. Even though the solute may be less soluble at the lower temperature, it does not always separate from the solution. A solution in this condition is called **supersaturated.** Such solutions of sodium thiosulfate may easily be made in the way just described. Supersaturated solutions also frequently occur when a slightly soluble substance is formed by chemical reaction in solution. Mixing ammonium hydroxide, ammonium chloride, sodium

phosphate and a magnesium salt, such as magnesium chloride or nitrate in aqueous solution ought to produce a precipitate of magnesium ammonium phosphate, $MgNH_4PO_4$, since this substance is very slightly soluble in water. Even if enough of the mixture is used to exceed the amount of magnesium ammonium phosphate in a saturated solution, the precipitate frequently fails to appear,—a supersaturated solution is formed.

Supersaturated solutions may be made to deposit their excess of solute in several ways. The simplest are to shake the solution vigorously, to scratch the vessel which is in contact with the solution, or to introduce into the solution a minute amount of the solid solute. These methods are just like those described for causing a supercooled liquid to crystallize. Possibly the explanation of supersaturation and of the effectiveness of the methods for overcoming this condition is the same as that tentatively given for supercooling. (See page 117.) It would, however, be difficult to apply this explanation to supersaturated solutions of gases which are quite commonly encountered. If, for example, a bottle of "carbonated water" is opened, the carbon dioxide escapes rapidly from the solution for a while. After evolution of the gas has apparently ceased, it can again be started by stirring the liquid. There are many other instances.

The phenomenon of supersaturation often causes difficulty in analytical work. Substances are very frequently detected by the precipitates they form with certain reagents. The formation of magnesium ammonium phosphate is used, for example, as a test for the presence of magnesium in solution. If only small amounts of magnesium are present, it may be overlooked because a supersaturated solution of the phosphate in question is formed. Before deciding that no magnesium is present, the mixture must always be vigorously stirred or the glass with which it is in contact be scratched with a glass rod.

Solubility.—The quantity of solute contained in a given quantity of the saturated solution is called the solubility of the solute. The solubility may be stated in any of the units mentioned for expressing the concentration of a solution. The ones most commonly used are (1) the number of grams of solute per 100

grams of solvent and (2) the solubility stated in terms of molar solutions.

The solubility of substances in given solvents is affected both by the pressure and the temperature. Suppose a given gas is in equilibrium with a solution of that gas in a given solvent. This statement merely means that the number of molecules of the gaseous substance entering the solution is equal to the number escaping from it. Suppose now, that the pressure of the gas is increased. This increases the number of molecules of gaseous substance which strike unit surface of the solution in unit time. Hence more molecules enter the solution than leave it, and the solution will become more concentrated. This discussion also shows that the solubility of the gas must be unaffected by the presence of other gaseous substances in the space above the solution. **The solubility of a gas at a given temperature is,** therefore, **directly proportional to its partial pressure.** This relationship is called **Henry's law.**

Again, assume that a gas is in equilibrium with its solution, but that the temperature is now raised without allowing the pressure to change. The speed of the dissolved molecules increases and more of them must escape from solution than did before. But no more molecules of the gas strike the surface than before, because the pressure of the gas is unchanged. Hence, more molecules leave the solution than enter it; the solution becomes more dilute. It is of course conceivable that rise in temperature might affect the relative attractive forces of the substances involved so as to counteract to a certain extent the effect just described, but quite generally the solubility of gases decreases with rise in temperature. By the term " solubility of a gas " is meant the solubility under a given partial pressure of the gas, usually 760 mm.

The effect of temperature and pressure on the solubility of solids and liquids in each other is much more complex. In general, change of pressure has little influence on the solubility, and may be neglected. Change of temperature in some cases influences solubility greatly, in other cases it has little effect; rise in temperature sometimes increases solubility, less often the reverse is true. For example, 100 grams of water at 0° C.

dissolves about 36 grams of sodium chloride; at 100° C. the amount dissolved is about 39 grams—a very slight difference. At 0° C. the same amount of water dissolves only 13 grams of potassium nitrate, but at 100° the quantity dissolved is 246 grams, an enormous increase. On the other hand the solubility of calcium hydroxide at 100° is only about half as great as at 20°. The fact that most substances are more soluble at high temperatures is partly responsible for the tendency of experimenters to heat a mixture of solute and solvent when making a solution, but irrespective of the effect of temperature on the solubility, rise in temperature always increases the rate of solution.

A very convenient method of recording solubilities of substances at various temperatures is by means of curves like those shown in Fig. 6. The solubilities are in grams of anhydrous solute per 100 grams of solvent. In general, the curves are smooth. Occasionally as, for example, in the case of sodium sulfate, the curve shows a sharp break. The point at which this break occurs represents the temperature at which the decahydrate of sodium sulfate, Glauber's salt, is in equilibrium with the anhydrous salt; the former is stable below and the latter above this temperature. The equilibrium temperature is called the **transition point,** and may be determined by finding the corresponding break in the solubility curve. Additional data, more accurate than those of the figure, are given in the table on the inside of the cover of the book. A rough survey of solubilities of various classes of compounds is found on page 466.

Extraction by Solvents. Law of Distribution.—If an aqueous solution of iodine is shaken with ether so that the two liquids become thoroughly mixed, and the mixture is then allowed to stand until the water and ether have again separated, a large part of the iodine originally present in the aqueous solution is found in the ether. In like manner, chloroform, carbon disulfide and other solvents in which iodine is soluble, **extract** the latter from aqueous solution. These are merely illustrations of a phenomenon which always occurs when a solution is shaken or otherwise well mixed with another liquid in which the solute is also soluble, provided the two liquids are not miscible with

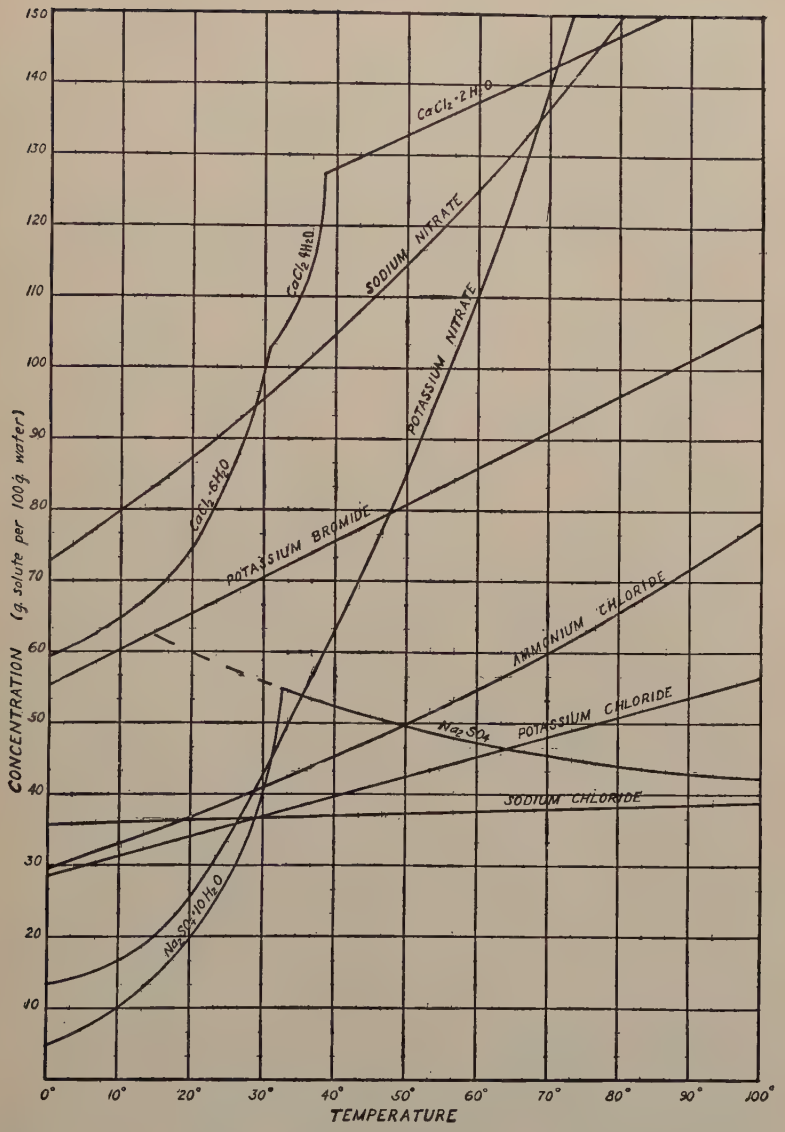


FIG. 6 — SOLUBILITIES IN WATER OF SEVERAL SUBSTANCES AT VARIOUS TEMPERATURES

The concentration of the saturated solutions is given in grams of solute per 100 grams of solvent (water).

each other. The substance distributes itself between the two solvents so that the ratio of its concentrations in the two solvents is the same as the ratio of its solubility in each of the two solvents, irrespective of the original concentration of the solution from which the substance is extracted.[1] This fact is called the **law of distribution.** Obviously, it is desirable to use for an extracting solvent, a liquid in which the substance is more soluble than in the liquid from which it is to be extracted; if this is not done, very large volumes of the extracting liquid and repeated extractions are necessary to remove the substance from the original solvent effectively. Extraction of substances by solvents from other solvents is much used in chemical work as a process of purification.

Vapor Tensions of Solutions.—It has been shown (page 109) that the vapor tension of a liquid is a measure of the frequency with which those of its molecules possessing a velocity greater than the average strike the surface and escape into the surroundings. Anything which prevents these fast moving molecules from reaching the surface lowers the vapor tension of the liquid. If a non-volatile solute is dissolved, its molecules must occasionally lie in the path of fast moving molecules of the liquid on their way to the surface. Some of the latter are therefore deflected and may not reach the surface at all, or may reach it much later than they would have if no solute had been present. These considerations explain not only why non-volatile solutes **lower the vapor tension of the solvent**, but also why the magnitude of the **lowering is proportional to the number of dissolved molecules.** The lowering of the vapor tension of a solvent by the solute may, therefore, be used as a measure of the molecular weight of the dissolved substance. Vapor tensions are difficult to measure; hence the method just outlined is not a very practical one for determining molecular weights, and need not be further discussed. But the lowering of the vapor tension of the solvent is closely related to other phenomena which lead to very simple methods for molecular weight determinations, and are of considerable practical importance.

[1] It is assumed that the formula of the substance is the same in both solvents.

Freezing and Boiling Points of Solutions.—The relationship of the vapor tensions of liquids to their freezing and boiling points has already been discussed, and is shown graphically in Figs. 4 and 5, pages 113 and 116. The curve representing the change of vapor tension of a solution with change in temperature is quite similar to that of the curve for the pure solvent, except that at all temperatures the curve for the solution lies below that for the pure solvent since at all temperatures the solution has the lower vapor tension. If the solute is soluble only in the liquid solvent, and not in the solid formed by freezing of the solvent, the vapor tension curve of the solid form of the solvent is not changed by the formation of the solution. The point at which this curve intersects the vapor tension curve for the solution lies to the left of the point of intersection of the vapor tension curves of solid and pure solvent, as shown in Fig. 7. In other words the **freezing point of the solution is lower than the freezing point of the pure solvent.**

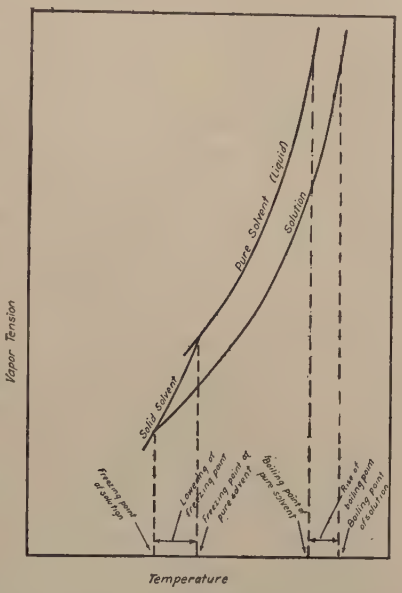


FIG. 7. — VAPOR TENSIONS OF LIQUID AND SOLID SOLVENT, AND OF A SOLUTION AT VARIOUS TEMPERATURES

In order to have both freezing point and boiling point on the same diagram an arbitrary scale is used.

Consideration of the meaning of the boiling point in terms of vapor tension shows that the **boiling point of a solution must be higher than that of the pure solvent, when the solute is non-volatile.** This may also be seen from the diagram of Fig. 7. At a certain temperature, T_b, the vapor tension of the pure solvent is 760 mm. At this temperature the vapor tension of the solution is lower, and therefore less than 760 mm. In order to reach the boiling point (which is the temperature at which

the vapor tension is 760 mm.) the temperature of the solution must be raised above the boiling point of the solvent.

Characteristics of the Freezing and Boiling Points of Solutions.—In the preceding paragraph, discussion of freezing points of solutions was limited to those cases in which the solute is non-volatile, and does not form a solid solution with the solid solvent. This need not be the case, but other types of solutions will not be discussed. The type of solutions to which the discussion is limited exhibits certain characteristics which deserve further description. When such a solution begins to freeze, the pure solvent crystallizes out provided the solution is not saturated. Hence, the solution must become more concentrated. The more concentrated the solution, the greater the lowering of the vapor tension, and therefore the greater the lowering of the freezing point. Hence, as the solution is cooled, the freezing point must fall. Ultimately, of course, the solution becomes saturated. Further cooling will cause precipitation of both solvent and solute, so that the concentration remains constant. The temperature at which this occurs is called the **eutectic point.** The behavior of the pure solvent on freezing is quite different—whereas the temperature of a freezing solution continuously falls until the eutectic temperature is reached, that of a freezing simple liquid remains constant. This is a convenient criterion for determining whether a given liquid is a pure substance or a solution.[1]

In a similar fashion, boiling a solution of a non-volatile solute increases the concentration of the solution. Increase in concentration means further lowering of the vapor tension, and therefore further rise of the boiling point. Thus, as the solution boils, the boiling point rises, in contrast to the behavior of a pure liquid whose boiling point at constant pressure is constant.

Facts Illustrative of the Lowering of Vapor Tension, Lowering of Freezing Point and Rise of Boiling Points of Solutions.—A

[1] It must be borne in mind that this criterion cannot always be safely applied because, in the first place, solutions of a certain (the eutectic) concentration do not behave in this way, and in the second place, solutions which deposit solid solutions of solute and solvent on freezing sometimes also behave like eutectic mixtures.

number of facts, well known even to the beginner in chemistry, can be explained by the phenomena just described. A few illustrations will be cited. Gases, like hydrogen chloride, which are very soluble in water fume in moist air. Moist air ordinarily contains minute droplets of water, too small to be seen by the naked eye. If such air is mixed with a very soluble gas, the latter dissolves in the droplets of water and forms a very concentrated solution, the aqueous tension of which is very much less than that of the water vapor in the air. Consequently (see page 110) water condenses on the droplets which thus increase in size and become visible as a fog or fume.[1]

Salt strewn on icy sidewalks on a moderately cold day **causes the ice to melt.** Possibly the ice is covered by an extremely thin layer of liquid water. In this the salt dissolves. The resulting solution has a vapor tension less than that of the solid ice; hence, the ice passes over into the liquid—it melts. (See page 116).[1] Addition of salt to the water in the radiator of an automobile prevents freezing of the water on moderately cold days. If a very soluble salt is used, freezing can be prevented even in very cold weather because the very concentrated solution has a very low freezing point. Unfortunately, most salts of this type have a corroding effect on the metal of the radiator, and are therefore not much used.

Deliquescence is a phenomenon explained in similar fashion. In moist air, any solid is probably coated with a very thin layer of liquid water. (See note to the preceding paragraph.) If the solid is soluble in water a saturated solution is formed. When the solid is extremely soluble in water, the resulting solution is very concentrated and has a very low vapor tension. This vapor tension may be lower than the pressure of the water vapor in the air. If so, water condenses on the solution, more solid dissolves until all of the material has gone into solution. Substances which exhibit this behavior are called **deliquescent.**

[1] It is probably not absolutely necessary, in explaining the fuming of hydrogen chloride or the effect of salt on ice, to assume that droplets of water exist in the air or a film of water on the ice. The fact that hydrogen chloride and salt are soluble in water is evidence that these substances attract each other, and this attraction may be sufficient to explain the formation of a solution.

Determination of the Molecular Weights of Substances in Solution.—It was pointed out above that the lowering of the vapor tension is proportional to the number of molecules of dissolved material present in a given volume of the solvent. The lowering of the freezing point and the rise of the boiling point are determined by the lowering of the vapor tension. Consequently the lowering of the freezing point and the rise of the boiling point must likewise vary with the number of dissolved molecules. Either of these quantities may, therefore, be used to calculate the relative number of solute molecules in a given volume (or weight) of a solvent, and hence to determine the molecular weight of the solute. The freezing-point method must be limited to solutions from which only the pure solvent crystallizes on freezing, and the boiling-point method to solutions of non-volatile solutes. Also, only very dilute solutions should be used when accurate results are desired, since the proportionality between the depression of the freezing point or the elevation of the boiling point and the number of dissolved molecules is an exact one only for such solutions.

The use of the freezing-point method for determining molecular weights may be illustrated as follows. One gram molecule of any solute [1] dissolved in 1000 grams of water lowers the freezing point of the latter 1.86°. Double the weight of solute in the same weight of solvent, or the same weight of solute in one-half the weight of solvent, produces twice the lowering, and so on. Suppose, for example, that 25 grams of solute in 200 grams of water lowers the freezing point by 0.62°. One hundred and twenty-five grams of solute in 1000 grams of solvent is a solution of the same concentration and will produce the same lowering of the freezing point—namely 0.62°. Since 0.62° is $\frac{1}{3}$ of 1.86° the amount dissolved per 1000 grams of solvent is but $\frac{1}{3}$ of a gram molecular weight. The latter must therefore be 3×125.

The number of degrees by which the freezing point of the solvent is lowered in a solution containing 1 gram molecular weight of solute per 1000 grams of solvent is called the **molecular lowering** of the freezing point and is a characteristic constant for every

[1] A type of apparent exceptions is discussed in Chapters XIII and XIV.

solvent. The rise of the boiling point may be used in similar fashion to determine molecular weights, and the number of degrees by which the boiling point is raised by 1 gram molecule of solute per 1000 grams of solvent is called the **molecular rise** of the boiling point. In the following table, numerical values for the molecular lowering of the freezing point and the molecular rise of the boiling point are given for a few solvents frequently used for molecular weight determinations. The freezing and boiling points of the pure solvents are also included. In general the freezing point method is the more commonly used of the two, since the boiling point of a liquid is greatly affected by changes in external pressure, and this is not the case for the freezing point.

TABLE VII

Molecular Lowering of the Freezing Point and Molecular Rise of the Boiling Point of a Few Solvents

Solvent	Freezing Point of Pure Solvent ° C.	Molecular Lowering of Freezing Point	Boiling Point of Pure Solvent ° C.	Molecular Rise of Boiling Point
Water	0.0	1.86°	+100.0	0.52°
Benzene (C_6H_6)	+5.5	5.12°	+ 80.2	2.57°
Phenol (C_6H_5OH)	+ 40.0	7.27°	+182.1	3.60°
Ether ($C_4H_{10}O$)	−117.0*	1.79°	+ 35.6	2.16°
Carbon tetrachloride (CCl_4)	− 24.7	2.98°	+ 78.5	4.88°

* Ether, because of its very low melting point, is seldom used for molecular weight determinations by the freezing point method. It is included in the list because it is a convenient solvent for the boiling point method. To a smaller extent the same is true of carbon tetrachloride.

The importance of the boiling point and freezing point methods is readily understood. There are many substances which cannot be volatilized without undergoing decomposition or which volatilize only at very high temperatures, so that the weight of 22.4 liters of the substance in gaseous form cannot be determined, and the molecular weight cannot be obtained by

the method based on Avogadro's law. (See Chapter V.) In these cases the solution method is the only one available. The study of the molecular weights of a certain class of substances dissolved in water or a similar solvent has led to such important discoveries that the results of these investigations will receive discussion in Chapter XIII.

Other Phenomena Aaccompanying the Formation of a Solution.—Heat effects are frequently noted when a solution is prepared. The resulting solution may be warmer than the original materials, i.e., heat is given off during the process of dissolution, or the reverse effect may occur. The bearing of this heat effect on the change of solubility with change in temperature will be discussed in Chapter XII. Volume changes also occur, i.e., the volume of the solution may be greater or less than the sum of the volumes of the original components. The student will encounter illustrations of all of these types of effects in his laboratory work—detailed discussion of them is unnecessary here.

EXERCISES

(1) (*a*) What is an emulsion? (*b*) What is the difference between a suspension and a solution? (*c*) What is a "solid solution"?

(2) What is the evidence that the molecular attractions which hold together the molecules of a solid are counteracted when the solid dissolves in a liquid?

(3) What is the explanation tentatively given in this text for the fact that substances of similar character often are soluble in each other?

(4) Define the terms: solute, concentrated, dilute, saturated solution.

(5) (*a*) How many grams of sodium sulfate (Na_2SO_4) are contained in 1 liter of a molar solution of the substance? (*b*) How many grams of copper nitrate ($Cu(NO_3)_2$) in 1 liter of a 1/10 molar solution?

(6) (*a*) How many grams of acetic acid ($H \cdot C_2H_3O_2$) are contained in 1 liter of a $\frac{1}{5}$ normal solution? (Acetic acid reacts with sodium hydroxide according to the equation: $HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$.) (*b*) How many grams of barium hydroxide are contained in 1 liter of a $\frac{1}{20}$ normal solution?

(7) A 77 per cent solution of sulfuric acid has a density of 1.7. (*a*) What is the normality of the solution? (*b*) What is the concentration of the solution in terms of molarity?

(8) Is a saturated solution necessarily a concentrated one?

(9) Describe several methods for causing supersaturated solutions to deposit the excess of dissolved material.

(10) (*a*) What is Henry's law? (*b*) Carbon dioxide at atmospheric pressure dissolves in its own volume of water at 15°. What volume of the gas, referred to standard conditions, would dissolve if the pressure were 4 atmospheres?

(11) Explain why gases become less soluble with rise in temperature.

(12) (*a*) Explain why a solution of a non-volatile solute has a lower vapor tension than the pure solvent. (*b*) Upon what is the magnitude of the lowering dependent?

(13) (*a*) Prove, both in words and by means of a plot showing the change in the vapor tension of the pure solvent and of the solution with change in the temperature, why lowering of vapor tension must produce a rise of the boiling point. (*b*) Upon what must the magnitude of the rise of boiling point depend?

(14) Answer as in (13), (*a*) and (13), (*b*) for the lowering of the freezing point.

(15) (*a*) Why may the lowering of the vapor tension, the lowering of the freezing point and the rise of the boiling point be used to determine the molecular weight of a dissolved substance? (*b*) Which of these methods is the simplest? Why?

(16) 30 grams of a substance dissolved in 1000 grams of water lower the freezing point by 0.93°? What is the molecular weight of the substance?

(17) Explain why hydrogen chloride fumes in air.

(18) Explain why salt sprinkled on ice causes the ice to melt on a moderately cold day. Why will it not do so on an intensely cold day?

(19) What sort of substances deliquesce? Why?

REFERENCES

MELLOR—Comprehensive Treatise, pages 574–577, Vol. I, gives a short summary of the history of views about the cause of solution. In the same volume pages 450 to 456 discuss the phenomena of supercooling and supersaturation.

CHAPTER XI

THE HALOGENS

THE HALOGENS.—OXIDIZING AGENTS.—HYDROGEN COMPOUNDS OF THE HALOGENS.—THE HALIDES

THE four elements, chlorine, fluorine, bromine and iodine are so similar in their properties that they have been grouped under the name, halogens, which means the salt producers. All of them are of great importance in all branches of chemistry, and their behavior illustrates a number of very important principles, the discussion of which is of fundamental importance to the student of chemistry. For these reasons it is necessary to take them up in some detail.

Chlorine is prepared by oxidation [1] of chlorides of which the most common and cheapest and, therefore, the one generally used is common salt, sodium chloride. The methods of oxidation may be divided into two classes, (1) by means of chemical reagents and (2) by means of electrolysis.

Oxidizing Agents.—In order to understand the principles involved in preparing chlorine by means of oxidizing agents, it must be borne in mind that chlorine itself is an oxidizing agent. Consequently the oxidizing agent used in preparing it must be a stronger oxidizer than chlorine itself, or else a large excess of an oxidizing agent, the oxidizing power of which is of the same order as that of chlorine, must be used. This is true, because reactions of oxidation and reduction are reversible. The point is illustrated best by the study of a reaction which was formerly used to prepare chlorine commercially.

When sodium chloride is treated with concentrated sulfuric

[1] Reactions of oxidation and reduction have already been referred to on pages 91, 93, 99, 102 (foot-note) and 132. Detailed discussion of this type of reaction will be found in later chapters.

acid, the gas hydrogen chloride is formed. This reacts with oxygen at elevated temperatures to give chlorine according to the equation:

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2.$$

But chlorine and steam will interact to give oxygen and hydrogen chloride. To indicate this, a double arrow ($\leftrightarrows$) has been used in writing this equation. As a result of the reversibility of the reaction, a state of equilibrium is reached.[1] At a temperature of about 600° C. this occurs when only 50 per cent of the hydrogen chloride has been converted into chlorine; at lower temperatures the conditions are more favorable to the formation of chlorine, since the reaction goes further to the right before the reverse action attains a speed equal to that of the forward action. At 400°, for example, a yield of 80 per cent can be obtained, but the reaction at this temperature is so slow that catalytic agents have to be employed. It is not necessary to discuss the practical details for manufacturing chlorine by this reaction since this method has been displaced by others that are more economical.

A table showing the relative strengths of oxidizing agents like the one showing the relative activity of metals would be very useful. If such a table were at hand, the oxidizing agents which could be used to make chlorine or the other halogens could readily be picked from it by choosing one which is sufficiently stronger than the halogen to be prepared. But that cannot be very satisfactorily done because the oxidizing strength of oxidizing agents is greatly affected by changes in external conditions. The influence of temperature has been illustrated in the reaction between oxygen and hydrogen chloride. Many other factors, particularly the nature of the solvent used, and the presence of acid or alkali, are of great importance. An interesting illustration of these effects is found in the behavior of hydrogen peroxide which oxidizes manganous salts to higher oxides of manganese [2]

[1] See pages 99–100.

[2] Manganous salts are derived from manganous oxide, MnO. The higher oxides of manganese contain a larger amount of oxygen for a given amount of manganese. Permanganates are derived from Mn_2O_7.

in the presence of alkali, but in acid solutions reduces permanganates to manganous salts. Because of these difficulties all that can be done is to classify some of the oxidizing agents roughly into large groups.

The most powerful oxidizing agent is elementary fluorine; permanganates and chlorates, particularly when in acid solutions, manganese dioxide and lead dioxide suspended in acids, and concentrated nitric acid are strong oxidizing agents. Chlorine likewise is a strong oxidizing agent, but all of those thus far mentioned liberate chlorine from chlorides under suitable conditions. Somewhat weaker oxidizing agents are concentrated sulfuric acid, chromates and dichromates in the presence of acids, and bromine. Still weaker are ferric salts in acid solutions, cupric salts and iodine. Of course these substances are but a few of a vast number which possess oxidizing powers, and the grouping which has been made is not an accurate one. It will be noted that oxygen has not been mentioned. For practical purposes it is somewhat difficult to place, because at ordinary temperatures oxygen frequently exerts its oxidizing power only in the presence of catalytic agents. Its position lies between that of chlorine and of bromine.

Preparation of Chlorine.—According to the foregoing, it follows that chlorine can be prepared by the action of the stronger oxidizing agents on chlorides. The reagents most commonly employed in the laboratory are manganese dioxide, potassium permanganate and bleaching powder, $CaOCl_2$.[1] All of them are used with solutions containing dilute sulfuric acid. Manganese dioxide has the advantage of cheapness and of giving a relatively large yield of chlorine from a small bulk of material. Bleaching powder is also inexpensive, is readily available, and reacts in the cold, while heat is necessary when manganese dioxide is used. Potassium permanganate is relatively expensive and is used when a small, definite amount of chlorine is required, because the reaction readily goes to completion and the amount of chlorine obtainable from a weighed amount of permanganate may therefore be calculated. The reactions of lead dioxide and of potassium or sodium chlorate with hydrochloric acid are also

[1] Also called chloride of lime. See page 376.

occasionally employed for special purposes. The reaction equations follow:

$$MnO_2 + 2NaCl + 2H_2SO_4 \rightarrow MnSO_4 + Na_2SO_4 + Cl_2 + 2H_2O$$

$$2KMnO_4 + 10NaCl + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 5Cl_2 + 8H_2O$$

$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$

$$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$$

$$KClO_3 + 6HCl \rightarrow KCl + 3H_2O + 3Cl_2$$

No chloride has to be used with bleaching powder because the latter is a chloride itself. The equation for the action of potassium chlorate represents but one of a number of possible reactions between the substances involved. Hydrochloric acid may be used in place of the mixture of sodium chloride and sulfuric acid, and *vice versa*, in all cases, but the mixture is cheaper.

For commercial purposes, chlorine is nowadays most frequently prepared by electrolysis of an aqueous solution of a chloride. When two platinum electrodes, connected respectively with the positive and the negative pole of a battery, are dipped into a concentrated solution of hydrochloric acid, hydrogen is generated at the negative pole and chlorine at the positive pole. This method is not a practical one because of the expense of the materials used. A somewhat similar reaction occurs when an aqueous solution of sodium chloride is electrolyzed. Chlorine is obtained at the positive pole; sodium hydroxide and hydrogen at the negative. The anode (positive pole) is made of graphite or, quite rarely, of an alloy of platinum and iridium, and the cathode (negative pole) is usually iron. Since the anode and cathode products react with each other, it is necessary to prevent their intermixture. This is accomplished in several ways—one of them is to interpose a diaphragm made of cement or sheets of heavy asbestos between the two poles. Both materials are porous and therefore allow the solution to pass through them so that the current can flow, but are nevertheless effective in

keeping the products of the reaction from mixing in appreciable amounts. Further details will be given when the manufacture of sodium hydroxide is described. (See page 475.)

Preparation of the Other Halogens.—Since fluorine is the most powerful oxidizing agent known it cannot be prepared by chemical oxidation of fluorides.[1] Consequently only an electrolytic method is possible. For many years all efforts to prepare the element proved unsuccessful because fluorine attacks water, and aqueous solutions of fluorides can therefore not be employed. It was finally obtained by Moissan by electrolysis of potassium fluoride dissolved in liquid hydrogen fluoride. A platinum vessel was used by him because he believed that fluorine would act on all other materials. As a matter of fact fluorine does act on all metals, but copper vessels may nevertheless take the place of platinum ones because copper rapidly becomes coated with a firmly adhering layer of copper fluoride, which protects the copper from further action by the fluorine. The use of molten acid potassium fluoride (KHF_2) has proved more practical than the use of a solution of potassium fluoride in liquid hydrogen fluoride. The fluorine is carried from the vessel after electrolysis through copper tubes.

For the preparation of the remaining two halogens, either chemical oxidation or electrolysis of the corresponding salts, i.e., bromides or iodides, may be used. Bromides are found in nature associated with chlorides in salt deposits, notably the famous Stassfurt potash beds, and in sea water. Considerable quantities of bromides are obtained also from the salt wells in the United States (chiefly in Michigan and Pennsylvania). Evaporation of the brines leads first to the deposition of chlorides, which are the less soluble salts; the bromides thus accumulate in the mother liquors. Chlorine is most commonly employed as the oxidizing agent for liberating the bromine; the reaction may be written

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

[1] A few fluorides are decomposed by heat to give free fluorine. The fluorides in question are too difficult to prepare to make practical their employment as a means of obtaining fluorine.

if the bromide is that of potassium. The mixture is heated and the bromine, being volatile, escapes from the liquor as a vapor, and is condensed by cooling. The bromine thus obtained is contaminated with chlorine and sometimes with iodine. For its purification the crude material is redistilled. The chlorine, which is more volatile than bromine, comes off first. Iodine is removed by precipitation as a copper salt.

Iodides, required for the preparation of iodine, are obtained from sea plants, notably kelp, and from the nitrate deposits [1] which contain a very small quantity of iodine compounds. The oxidizing agent used to liberate the iodine from these depends upon the nature of the iodine compound. If it is an iodide, manganese dioxide and dilute sulfuric acid are used. The natural iodides always contain chlorides and bromides. Since iodides are the most readily oxidized, iodine will be liberated before the manganese dioxide acts on the bromide or chloride. By carefully regulating the amount of the reagents, fairly pure iodine is obtained. The equations for the reaction of manganese dioxide on iodides and bromides are exactly like that for the action on chlorides. In large scale operations, perfect regulation of the quantity of the reagents in the process is difficult to secure; commercial iodine is therefore likely to be contaminated with bromine and chlorine. For its purification, crude iodine is mixed with a little potassium iodide and sublimed. The reasons for the effectiveness of this procedure will become apparent when the properties of the elements involved have been studied.

From what was said on page 148 about the relative oxidizing powers of bromine and of iodine, it follows that there are many oxidizing agents which could be used to liberate these elements from their salts. Any of the oxidizing agents which liberate chlorine liberate the other two; in addition to those oxidizing agents, chlorine (as already mentioned), concentrated sulfuric acid, or chromates in acid solution liberate bromine or iodine; and chlorine, bromine, ferric and cupric salts liberate iodine. Although some of these reagents are occasionally employed in the laboratory they are not generally found practical for one reason or another.

[1] See page 314.

Physical Properties of the Halogens.—The following table contains a summary of the most important physical properties of the halogens:

TABLE VIII

PHYSICAL PROPERTIES OF THE HALOGENS

	FLUORINE	CHLORINE	BROMINE	IODINE
Atomic weight *....	19.0	35.46	79.22	126.92
Density †.....	1.69	3.22	3.188	4.933
Freezing point.....	−233°	−102°	−7.3°	116.1°
Boiling point.....	−187°	−33.8°	59°	184.35°
Solubility in water ‡	.....	9.61	4.3	0.32

* Atomic weights, although not physical properties, are included as a matter of convenience.

† The densities of the two gaseous elements, fluorine and chlorine, are the weights per liter at S. C., while for liquid bromine and solid iodine the weights of 1 c.c. at 0° are given.

‡ Solubility in water is given in terms of grams of solute per 100 grams of water at 0°, 760 mm.

The data on boiling and melting points in the table show that fluorine and chloride are gases, bromine a very volatile liquid, and iodine a solid at ordinary temperatures. All of the elements possess a penetrating odor, and injure animal tissues with which they come into contact. Bromine in particular causes severe burns, probably because, being a liquid, it comes into better contact with the skin or other exposed parts. It is very dangerous to inhale any of them, the danger being least with iodine which is relatively nonvolatile at ordinary temperatures. The elements all possess characteristic colors. Fluorine is pale yellow, chlorine greenish yellow, bromine reddish brown, and iodine black in the solid condition and violet as a vapor.

The behavior of iodine when heated is of interest. Solid iodine even at temperatures considerably below its melting point has a fairly high vapor tension. As a result, evaporation is rapid, and unless special precautions are taken to prevent it, the solid evaporates completely before it reaches the melting point. The passage of a solid directly into the vapor without melting is called **sublimation.**

In connection with the data on solubility, it should be noted that the halogens are more soluble in certain organic solvents than they are in water. Carbon disulfide, chloroform, carbon tetrachloride, and ether are capable of dissolving relatively large amounts of all except fluorine, which reacts with most solvents. Iodine forms two kinds of solutions—in the first three solvents just named the solution is of a deep violet hue, while aqueous, alcoholic or ethereal solutions are brown. It is believed that in the brown solutions, iodine enters into loose combination with the solvent, while in the violet solutions the iodine is present as such.[1]

Iodine is much more soluble in aqueous solutions of iodides, such as potassium iodide, than in pure water. The resulting solution is dark brown. The increase in solubility brought about by the iodides is probably due to the formation of compounds such as potassium tri-iodide, KI_3. Their nature is not yet thoroughly understood. Similarly, chlorides and bromides also increase the solubility of chlorine and bromine respectively. In fact any halogen salt increases the solubility of any one of the halogens, probably because compounds such as $KClI_2$, etc., are formed.

The most important observation to be made from the study of the physical properties of the halogens is the progressive change in properties with change in atomic weight. With increasing atomic weight the color deepens, the freezing and melting points rise, and the solubility in water decreases. A similar progressive change will be noted in the chemical properties.

Chemical Properties of the Halogens.—The densities of the elementary halogens in gaseous form and the freezing points of solutions containing them show that their molecules consist of 2 atoms in each case. These molecules are very stable. The extent of decomposition of fluorine by heat is so slight that it has not yet been determined; in order to decompose 50 per cent of the chlorine molecules into atoms a temperature of approximately 2600° is required, for bromine the corresponding temperature is about 1550°, and for iodine 1300°. In spite of the stability

[1] A saturated aqueous solution of chlorine is called "chlorine water," a similar solution of bromine, "bromine water."

of their molecules, the elements are very reactive as may be seen from the following list of some of their most important chemical properties.

The Halogens React with Metals.—Fluorine and chlorine react with all metals. With the more active metals such as the alkalies and the alkaline earths, the reactions are violent; metals such as iron or antimony, in finely divided form, react with evolution of sufficient heat to cause the solid material to glow brightly. Fluorine reacts with the least active metals, such as gold [1] or platinum, only when they are finely divided, and chlorine reacts with platinum very little except in the presence of chlorides such as sodium or hydrogen chloride. The function of these substances will be explained later. In general, fluorine reacts more vigorously and readily than chlorine. Bromine and iodine act less readily, iodine being the least active in this respect. Neither bromine nor iodine reacts with platinum or gold, but they do react with even so relatively inactive an element as mercury. The products of the reactions of the halogens with metals are the **halides.** Thus fluorine produces fluorides, chlorine chlorides, and so on.

Behavior toward Non-metallic Elements.—None of the halogens unites directly with the helium group of elements,[2] with nitrogen or with oxygen, although compounds of nitrogen and of oxygen with each of the halogens, except fluorine, can be prepared by roundabout methods. Fluorine is the only one which reacts directly with carbon, and this only if the latter is finely divided. Carbon compounds of all the halogens can be prepared indirectly. Fluorine and chlorine react with all of the other common non-metals; bromine and iodine act with fewer of the non-metals, and do not react so energetically.

As will be shown in a later chapter, the halogens act as **oxidizing agents** in all of these reactions, and the differences noted are due to differences in activity in this respect. The decrease in oxidizing power from fluorine to iodine is responsible

[1] The product of interaction of gold and fluorine has not been isolated, but the mechanical changes which gold undergoes when heated in fluorine indicate the temporary formation of an unstable compound.

[2] See Chapter XIX.

also for the different types of compounds produced when the various halogens react. Thus when fluorine acts on sulfur, sulfur hexafluoride, SF_6, is formed; chlorine gives sulfur tetrachloride, SCl_4, and sulfur monochloride, S_2Cl_2; bromine gives only sulfur monobromide, S_2Br_2; while iodine forms no compound with sulfur. Fluorine readily forms phosphorus pentafluoride, PF_5, although if an excess of phosphorus is present the trifluoride can be obtained; chlorine and bromine form the pentachloride or bromide only in the presence of an excess of halogen; and iodine forms no pentaiodide of phosphorus at all —only the compounds P_2I_4 and PI_3 are known. Similar phenomena are observed in the reactions of the halogens toward the metals. The metals are likely to exhibit their maximum valence when they react with fluorine or chlorine, while this does not happen so uniformly with bromine and much less frequently with iodine. The connection between valence and oxidation has already been mentioned;[1] it will be discussed in great detail in later chapters.

Displacement.—Chlorine reacts with many compounds by displacement, i.e., it liberates one of the elements of the compound and takes its place. For example it reacts with bromides and iodides as shown by the equations:

$$2KBr + Cl_2 \rightarrow Br_2 + 2KCl \quad \text{and} \quad 2KI + Cl_2 \rightarrow I_2 + 2KCl$$

It displaces carbon from many carbon compounds, particularly from hydrocarbons, under suitable conditions. For instance, turpentine, $C_{10}H_{16}$, catches fire when slightly warmed in an atmosphere of chlorine and burns with a smoky flame. The reaction results in the liberation of carbon (as soot or smoke) and the formation of hydrogen chloride, as shown by the equation:

$$C_{10}H_{16} + 8Cl_2 \rightarrow 10C + 16HCl$$

Similar reactions occur with other hydrocarbons. Fluorine displaces all of the other halogens from their halides, bromine displaces only iodine from iodides. Fluorine does not usually react by displacement with carbon compounds because it can

[1] See page 146, footnote.

combine with the carbon which would be set free by such a reaction; bromine rarely acts by displacement with carbon compounds and iodine practically never.[1]

Reactions with Water.—Fluorine reacts violently with water as shown by the equation:

$$3F_2 + 3H_2O \rightarrow 6HF\ ^{(2)} + O_3$$

The formation of ozone when oxygen would be expected is a phenomenon for which no explanation has been found. Chlorine reacts with water in three different ways. At low temperatures (below 10°) it unites with water to form the **hydrate**, $Cl_2 \cdot 8H_2O$; at slightly higher temperatures it reacts to give hydrochloric and hypochlorous acids,

$$Cl_2 + 2H_2O \leftrightarrows HCl + HOCl$$

At still higher temperatures or under the influence of light the reaction is

$$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2\ ^{(3)}$$

The second reaction is a reversible one. Equilibrium is attained at room temperature when only a very small fraction of the chlorine has reacted so that unless either the hypochlorous or the hydrochloric acid is removed very little of the chlorine will be used up. Nevertheless a solution of chlorine in water loses all of its chlorine in a relatively short time; this occurs because hypochlorous acid, especially in the light, decomposes into hydrochloric acid and oxygen. The reactions of chlorine and of fluorine with water, in which oxygen (or the corresponding substance ozone) is liberated, may be considered displacements. In these reactions, the more active oxidizing agent sets free the less active one, as is to be expected.

Bromine and iodine also react with water according to equations analogous to the one given for the second reaction of

[1] The displacement of carbon is probably a reaction of different type from the displacement of the halogens by each other, and may include substitution reactions (see below) as intermediate steps.

[2] For the formula of hydrogen fluoride, see page 162.

[3] It is probable that the formation of oxygen is due to decomposition of hypochlorous acid according to the equation, $2HOCl \rightarrow 2HCl + O_2$.

chlorine with water, but the equilibrium point lies very far to the left-hand side of the equation. Br_2, like chlorine, gives a hydrate, $Br_2 \cdot 10H_2O$, which decomposes at temperatures above 6°.

Substitution.—Many compounds containing hydrogen react with fluorine or chlorine in such a way that one atom of the halogen molecule combines with the hydrogen, and the other atom takes the place of the hydrogen in the compound. Such reactions are called **substitutions.** In displacements the element which is driven out of the compound remains uncombined, while, in substitutions, the substituent not only replaces another element in the compound but also combines with the element so removed. Substitution reactions may be illustrated by the behavior of methane toward chlorine. The following reactions occur:

$$CH_4 + Cl_2 \rightarrow HCl + \underset{\substack{\text{monochlor-}\\\text{methane}\\\text{or methyl}\\\text{chloride}}}{CH_3Cl}$$

$$CH_3Cl + Cl_2 \rightarrow HCl + \underset{\text{dichlormethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \rightarrow HCl + \underset{\text{chloroform}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \rightarrow HCl + \underset{\substack{\text{carbon}\\\text{tetrachloride}}}{CCl_4}$$

External conditions, such as temperature, intensity of illumination or nature of the catalytic agents present, determine which one of these products is obtained in any given experiment. When not all of the hydrogens are removed, the reaction is one of partial substitution; if all of them are removed complete substitution is said to have taken place. It is of course not necessary in the latter case to assume that all of the intermediate steps have actually occurred; thus for the formation of carbon tetrachloride one might write the equation:

$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$$

Fluorine is most active as a substituent; bromine acts less rapidly and completely than fluorine or chlorine, and iodine practically not at all by substitution.

Addition.—The halogens frequently unite directly with unsaturated compounds. (See page 99.) An interesting illustration is the reaction of chlorine with carbon monoxide to form carbonyl chloride, or phosgene, $COCl_2$, which was used as a poisonous war gas. Further illustrations are given in the chapter on carbon.

Reactions with Hydrogen.—Fluorine reacts with hydrogen with explosive violence to form hydrogen fluoride, HF (more commonly written H_2F_2, see page 162). Chlorine reacts explosively in direct sunlight, rapidly in diffused light, and extremely slowly in the dark. The product of the reaction is hydrogen chloride. Hydrogen bromide, HBr, is formed by interaction of the elements with appreciable rapidity only in the presence of catalytic agents, and hydrogen iodide is formed very slowly and incompletely under any conditions.

The Starch-iodine Reaction.—The addition of even minute amounts of iodine to a suspension of starch in water (starch emulsion or paste) causes the immediate appearance of an intensely blue color. It is so dark that if larger quantities of iodine are used, the mixture looks black. The reaction is used as a test for iodine; its sensitiveness is increased by the addition of potassium iodide to the starch emulsion. The phenomenon, which is characteristic of iodine and does not occur with any of the other halogens, is not understood; some investigators are of the opinion that a compound is formed, while the majority believe that the starch merely causes colloidal dispersion of the iodine. (See Chapter XXIX.)

Valence of the Halogens.—The halogens, in the reactions thus far listed, act uniformly with a valence of one. As will be seen in a later chapter, they are capable of forming other types of compounds in which they exhibit different valences. Discussion of these reactions and compounds has been deferred until the fundamental meaning of valence has been discussed.

Hydrogen Compounds of the Halogens. The Halides

Hydrogen Compounds. Methods of Preparation.—Although both fluorine and chlorine combine readily with hydrogen, the

hydrogen compounds of these elements are not prepared by this reaction because of the explosive violence with which it is likely to take place, and because of the cheaper methods available. In each case the action of concentrated sulfuric acid on a salt of the corresponding halogen is used. The most common fluoride is calcium fluoride, which is found fairly extensively in the form of the mineral fluorite, or fluorspar. The reaction equation is:

$$H_2SO_4 + CaF_2 \rightleftarrows CaSO_4 + 2HF$$

Sodium chloride is, of course, used to prepare hydrogen chloride:

$$NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + HCl$$

The salt is mixed with the acid and heated. When hydrogen fluoride is prepared, cast iron vessels must be employed or, for small scale operations, lead vessels, since hydrogen fluoride acts on glass or earthenware. Hydrogen chloride may be made in small quantities in glass vessels since it does not attack the glass; of course for large scale operations glass is too expensive, and other materials are employed. It is frequently convenient in the laboratory to cover the salt with a concentrated aqueous solution of hydrogen chloride before adding the sulfuric acid, in order to make the rate of reaction more uniform. If an excess of sodium chloride and higher temperatures are used the reaction proceeds as follows:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

The reactions for making the two hydrogen compounds just discussed are reversible. The reversibility is of no practical importance because both hydrogen fluoride and hydrogen chloride are almost insoluble in warm concentrated sulfuric acid, and therefore escape as gases from the field of the reaction. That the reactions are really reversible may, however, be demonstrated by slightly altering the conditions. If a saturated solution of sodium hydrogen sulfate is saturated with hydrogen chloride, sodium chloride crystallizes out—in other words, the reverse reaction occurs.

One might expect that gaseous hydrogen bromide and hydrogen iodide could be made by methods analogous to those described above. It has, however, been pointed out that sulfuric acid is a stronger oxidizing agent than either bromine or iodine, and that it liberates these elements from their compounds. Consequently, if sulfuric acid were used in the preparation of the other two acids, the latter would be oxidized as soon as formed.[1] There are several methods for preparing the two hydrogen compounds. Hydrogen bromide may be made by direct union of the elements in the presence of finely divided platinum (usually deposited on asbestos wool) which acts as a catalytic agent. A more convenient method consists of the action of bromine on naphthalene ($C_{10}H_8$). The products are various substitution products of naphthalene and hydrogen bromide. Another common method is the action of bromine on moist red phosphorus. The reaction is sufficiently described by the equations:

$$2P + 3Br_2 \rightarrow 2PBr_3$$ [2]

and

$$2PBr_3 + 6H_2O \rightarrow 2H_3PO_3 + 6HBr$$

The phosphorus tribromide is not isolated in the reaction, but is permitted to react at once with the water present to give phosphorous acid (H_3PO_3) and hydrogen bromide. To prevent too violent a reaction, the phosphorus is mixed with sand. For the preparation of hydrogen iodide, a similar reaction is employed. In this case the iodine and phosphorus are mixed in a dry flask and water dropped slowly on the mixture.

If only aqueous solutions of hydrogen bromide or of hydrogen iodide are required instead of the anhydrous gaseous substances, simpler methods may be employed. For the preparation of hydrogen bromide, a mixture of slightly diluted sulfuric acid and a saturated aqueous solution of potassium bromide are heated. The constant boiling mixture of hydrogen bromide and water

[1] The oxidation of hydrogen bromide and of hydrogen iodide is discussed in detail on page 285.

[2] PBr_5 may be formed under certain conditions. This reacts with water to give phosphoric acid, H_3PO_4, and HBr.

(see below) distills off and may be collected.[1] An aqueous solution of hydrogen iodide cannot be satisfactorily prepared in the analogous fashion, for even the diluted sulfuric acid decomposes hydrogen iodide. A satisfactory method consists of passing hydrogen sulfide through a suspension of iodine in water. The reaction is:

$$H_2S + I_2 \rightarrow 2HI + S$$

The sulfur is removed by filtration, and the solution concentrated by distillation; the hydrogen iodide cannot, however, be separated from water for reasons to be described below.

Both hydrogen bromide and hydrogen iodide may be prepared by the action of concentrated phosphoric acid on bromides and iodides respectively, but the reactions are too slow for practical purposes.

TABLE IX

Physical Properties of the Hydrogen Compounds

	HF *	HCl	HBr	HI
Freezing point	−92°	−112°	−88°	−51°
Boiling point	+19°	− 83°	−67°	−34°
Density	.....	1.641	3.608	.....
Concentration of constant boiling mixture	35%	20.2%	47%	57%
Boiling point of this mixture	120°	110°	126°	127°

* The formula of hydrogen fluoride is discussed below.

Temperatures are stated in this table to the nearest whole number. Densities refer to the weight in grams of 1 liter of the gaseous substance at 0°, 760 mm. The other terms will be explained below. All of the compounds are extremely soluble in water. One cubic centimeter of water dissolves about 525 c.c. of hydrogen chloride at 0° and 440 c.c. at 20°, and the solubilities of the other compounds are of the same order. Because

[1] This method has been worked out by Dr. H. N. McCoy but apparently has not been published.

of the high concentration of the saturated solutions, the gases fume when exposed to moist air as explained on page 141.

Formula of Hydrogen Fluoride.—With the exception of hydrogen fluoride, the hydrogen compounds have formulae analogous to HCl, as is shown by their percentage compositions and by the weights of 22.4 liters. The case of hydrogen fluoride is complicated. The composition of the substance indicates that the formula must be H_xF_x. The weight of 22.4 liters at temperatures above 90° agrees with the formula HF, but as the temperature is lowered the density increases much more rapidly than it ought to according to the gas laws. This suggests that molecules of the substance are uniting with one another to form heavier molecules—that **association** is occurring. At low temperatures the density of the gas corresponds to a molecular weight more than twice as large as that of HF. It was at one time believed that these facts meant that hydrogen fluoride gas at the lower temperatures is a mixture of molecules of H_2F_2 and H_4F_4. Recent experiments and calculations have shown, however, that the molecular species present are HF and H_6F_6.

The idea that hydrogen fluoride might in part consist of molecules of H_2F_2 was considered to gain support from the fact that compounds of the type of KHF_2 are known. It has been shown, however, that in moderately dilute solutions of hydrogen fluoride in water, only the substance HF exists and that the simple salts have formulae corresponding to KF. The existence of substances like KHF_2 must be ascribed to "complex ion formation," which will be described later. Similar compounds are known for chlorides, and yet the formula, H_2Cl_2, is not used for hydrogen chloride. No adequate reason to employ other than the simple formula, HF, for hydrogen fluoride therefore exists.[1]

Solutions of Constant Boiling Point.—When a very concentrated aqueous solution of hydrogen chloride is boiled, the vapor contains chiefly hydrogen chloride. As a result, the

[1] Experimental methods, not described in this text, for determining the molecular weights of substances in the liquid state lead to the conclusion that in liquid hydrogen chloride and in the other liquid hydrogen halides molecules of molecular weight greater than that corresponding to the simplest formula exist.

remaining solution becomes more and more dilute. When on the other hand, a very dilute solution of hydrogen chloride is boiled, practically only water evaporates, and the remaining solution becomes more concentrated. The result of boiling a concentrated and a dilute solution, therefore, is to cause the concentrations of the two to approach each other. There must, consequently, be a solution of intermediate concentration which, on boiling, gives off water and hydrogen chloride in such proportions that the concentration of the liquid does not change at all. In other words, the vapor must be a mixture of the same composition as the liquid from which it evaporates. Since the boiling point of a solution depends on its concentration, a solution which boils without change in concentration must have a constant boiling point, and must yield a distillate of the same composition as that of the original liquid. The behavior of such a solution on boiling is like that of a compound, and the constant boiling mixture of hydrogen chloride and water was once thought to be a compound with the formula $HCl \cdot 8H_2O$. But the composition of the constant boiling mixture does not correspond exactly to that of a substance of this formula, and, when the boiling is carried out at a pressure other than 760 mm., the composition of the constant boiling mixture is changed. The composition of a true compound is, of course, independent of the pressure at which it is boiled. In fact all volatile substances the vapors of which are very soluble in the solvent used form such constant boiling mixtures. The compositions and boiling points at 760 mm. of the constant boiling mixtures of each of the hydrogen halides and water are given in the table of physical properties above.

Chemical Properties of the Anhydrous Hydrogen Compounds.—The behavior of the hydrogen compounds in the absence of water, or similar solvents, is entirely different from their behavior in aqueous solution. The dry gases are quite stable. At 325° C. the degree of dissociation of hydrogen fluoride into its elements is not measurable, that of hydrogen chloride has been calculated to be about 0.0000015 per cent, that of hydrogen bromide 0.0035 per cent and that of hydrogen iodide 18.9 per cent. Only the last named is therefore appreciably decomposed at this tempera-

ture. All four are relatively inactive. When perfectly dry they act very slowly on the more active metals at high temperatures; carbonates and most oxidizing agents are not acted on under ordinary conditions. Except for reactions of organic chemistry which are not to be taken up in this text, the dry hydrogen halides are inert substances.

Chemical Properties of Aqueous Solutions of the Hydrogen Compounds.—The behavior of the aqueous solutions of these compounds presents a striking contrast to their lack of activity in the dry condition. These solutions are the strongest acids which are known. Strong acids possess the following chemical characteristics: they act on the more active metals, liberating hydrogen (see page 96); they react with bases, neutralizing them and forming the corresponding salts; they act by double decomposition (see page 165); they act on carbonates, liberating carbon dioxide as illustrated by the reaction:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

The reaction with carbonates is simply one of a type—strong acids displace weaker acids from their salts. Carbon dioxide is formed by the decomposition of carbonic acid, which was liberated from the carbonate by the stronger acid, hydrochloric acid. Another illustration is the liberation of the weak (very poisonous) acid hydrogen cyanide, or prussic acid, from potassium cyanide:

$$KCN + HCl \rightarrow HCN + KCl$$

In all of these respects, the aqueous solutions of the hydrogen compounds of the halogens, except hydrogen fluoride, are strong acids. These solutions are therefore called hydrochloric, hydrobromic and hydriodic acid respectively. Their action on oxidizing agents has already been discussed, and the only additional statement necessary is that the reactions, mentioned in the discussion, are essentially reactions of their aqueous solutions.

The behavior of **hydrogen fluoride** requires special treatment. Its aqueous solution (called hydrofluoric acid) is not nearly so strong an acid as are the solutions of the other hydrogen compounds. It is therefore not nearly so reactive toward

metals, alkalies, carbonates and salts of weak acids. Hydrogen fluoride, either by itself or in solution, acts on silicon dioxide and on silicates. Since glass, porcelain and other similar materials consist largely of silicates, this property of hydrogen fluoride acquires considerable significance. Solutions of the acid cannot be kept in glass vessels, and consequently hard rubber or wax bottles, dishes or funnels must be employed in reactions in which hydrofluoric acid is used. Of course the less active metals like gold and platinum would be suitable, but they are expensive. Lead also is resistant to the action of the acid, and is occasionally employed. On the other hand, this ability to react with silicates makes the acid quite useful in several ways. It is used for etching glass—the part to be etched is left uncovered while the rest is coated with paraffin, and then either aqueous hydrofluoric acid or its fumes are brought into contact with the object. The chemical reaction involved in this action is very similar to that which occurs when hydrofluoric acid acts on silicon dioxide:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

The volatile silicon tetrafluoride escapes. When silicates, like calcium silicate, $CaSiO_3$, are acted upon, fluorides like calcium fluoride are formed, in addition to the other products shown in the preceding equation. Hydrofluoric acid is useful also in chemical analysis. Many minerals are silicates, and are difficult to dissolve. They are often decomposed by the acid and converted into soluble compounds.

The behavior of hydrogen fluoride and fluorides toward oxidizing agents has already been discussed (page 150).

The Halides

Compounds of the halogens with the metals are called halides. They are salts and possess the properties characteristic of this type of compounds. The characteristic reactions of salts are double decompositions. These are reactions of the type:

$$AB + CD \rightleftarrows AD + CB$$

and are familiar to all who have studied elementary chemistry. As will be shown in later chapters, such reactions are reversible and can be driven to completion in one direction or another only by the removal of some component of the system. The simplest method of doing this is by the formation of an insoluble product. Hence it is of interest to know which of the halides are insoluble in water. Of the common fluorides, the calcium salt, CaF_2, is the least soluble one; barium, strontium, magnesium, zinc and lead fluorides also are but slightly soluble in water. Of the other halides, the silver salts are the least soluble; mercurous salts and lead [1] salts are also slightly soluble. The chlorides are the most soluble, and the iodides the least soluble of the salts named.

Summary.—The preceding discussion of the halogens and some of their compounds has brought out several points of great importance in chemistry. In the first place the halogens are among the most important substances employed in chemical industry. Chlorine is one of the most commonly used oxidizing agents. It owes to this property its use as a bleach and as a disinfectant. Bromine is largely used as an oxidizing agent and in organic chemistry for the preparation of many compounds; iodine is an important disinfectant and antiseptic, and is used a great deal in organic chemistry. The halogen acids find important use, as is known to every student of elementary chemistry; the halides are the common salts.

But not only is knowledge of the practical side of chemistry enriched by the study of the halogens. Many of the facts in the preceding discussion require explanation, and these explanations will lead to an understanding of fundamental concepts. Most important perhaps is the finding of an explanation for the very striking fact that the properties, physical and chemical, of the halogens and of their compounds show a very regular change from the element of smallest to the one of largest atomic weight. This regularity cannot be accidental—its explanation is to be found only in an understanding of the constitution of the elements themselves. Another problem of great importance met with in this chapter is that of oxidation and reduction.

[1] Lead chloride is quite soluble in hot water, slightly soluble in cold.

What really are these reactions and why are some substances stronger oxidizing agents than others? A third question of equal importance is brought up by the fact that the hydrogen compounds of the halogens are inert when dry, and among the most active of compounds when in aqueous or similar solutions. The progress made in solving these problems will be described in the succeeding chapters.

EXERCISES

(1) (*a*) Illustrate by means of the reaction between hydrogen chloride and oxygen how the relative oxidizing power of two substances may be influenced by changes in temperature. (*b*) Show how the absence of a suitable catalyst for a reaction may lead to incorrect results about the relative oxidizing powers of substances.

(2) (*a*) Judging by the list of oxidizing agents given on page 148, what substances might be used to oxidize bromides to bromine in the presence of chlorides, without oxidizing the latter? (*b*) Which substances might be used to oxidize iodides to iodine without oxidizing bromides or chlorides? (*c*) With the answers to parts (*a*) and (*b*) in mind, work out a method of preparing iodine, bromine and chlorine in a fairly pure condition from a mixture of iodides, bromides and chlorides.

(3) Mention three chemical reactions by means of which chlorine may be prepared, and write the corresponding equations.

(4) Calculate the weight of chlorine obtained by complete interaction of (*a*) manganese dioxide; (*b*) potassium permanganate on 100 g. of sodium chloride in the presence of an excess of sulfuric acid.

(5) Explain why sodium chloride is not necessary in making chlorine from bleaching powder by the action of sulfuric acid.

(6) Describe the commercial method of preparing chlorine.

(7) Why can fluorine be prepared only by electrolysis of molten fluorides or of fluorides dissolved in hydrogen fluoride?

(8) (*a*) Give methods for the preparation of bromine and of iodine. (*b*) Compare these methods with those for the preparation of chlorine.

(9) (*a*) Considering the fact that iodides as found in nature are usually contaminated with chlorides and bromides, what are the most probable impurities of commercial iodine? (*b*) Why does heating the iodine with potassium iodide purify the element?

(10) Describe the regularities in changes of the physical properties

of the elements of the group, when they are arranged in the order of ascending atomic weights.

(11) (*a*) Define the term "sublimation." (*b*) To what other property is the ability of a solid to sublime related?

(12) (*a*) Judging from the statement made concerning the formulae of halogens what must be the approximate weight of 1 liter of gaseous fluorine and of 1 liter of gaseous chlorine? (*b*) Why are the values calculated by you only approximately correct? (*c*) Is the value for chlorine or the one for fluorine likely to deviate most from the experimentally determined value?

(13) It is pointed out in the text that iodine is the least stable of the elementary gases of the group. Into what does it decompose when heated?

(14) Write equations for the reactions of chlorine with each of the following metals: sodium, calcium, aluminium, antimony, copper, silver. If you are not familiar with the formulae of the resulting compounds, look them up in the chapters dealing with the metals in question, or look up the valences of the metals and deduce from them the formulae of the chlorides. (See Table V, page 105.)

(15) When chlorine acts on iron, does it form ferrous or ferric chloride?

(16) Illustrate the statement that bromine and iodine display somewhat less activity toward metals than do fluorine and chlorine.

(17) (*a*) Give several illustrations of the action of the halogens toward non-metals. (*b*) Illustrate by their behavior toward non-metals that fluorine and chlorine are stronger oxidizing agents than bromine and iodine.

(18) Distinguish between the terms "displacement" and "substitution." Write equations for reactions illustrating each type of reaction.

(19) In what three ways does chlorine react with water, and under what conditions does each of these reactions occur?

(20) Explain why, if chlorine reacts with water, it is nevertheless possible to have a solution of chlorine in water.

(21) (*a*) Compare the behavior of bromine and of iodine toward water with that of chlorine. (*b*) Contrast the behavior of fluorine toward water with that of the other halogens.

(22) Explain why chlorine water when exposed to sunlight loses all of its chlorine.

(23) Contrast the behavior of the four elements of the group toward hydrogen.

(24) Make a tabular outline in which methods of preparation, physical properties and chemical behavior of the halogens are summarized. It is

convenient to make this outline on fairly large sized paper and to have five columns: the first column to indicate the property and the four remaining columns to give data concerning each element with respect to this property. For example:

Property	Fluorine	Chlorine	Bromine	Iodine
color	pale yellow	greenish yellow	red	black (solid) violet (vapor)

By going over the chapter page by page, make certain that the outline is complete.

(25) Describe briefly the method of preparing hydrogen chloride and hydrogen fluoride and write equations for each.

(26) Why can the method described in answer to question (25) not be used to prepare anhydrous hydrogen bromide or hydrogen iodide?

(27) Give two methods for preparing hydrogen bromide conveniently.

(28) Give a method for preparing hydrogen iodide in gaseous form, and one for preparing a solution of hydrogen iodide in water. Write equations.

(29) Judging from the formula of hydrogen bromide, what must be the percentage composition of the substance? (Note that this problem is the reverse of the method for actually finding formulae. In addition to the percentage composition, what other data were needed to determine the formula definitely?)

(30) What are the arguments in favor of, and what those opposed to the formula H_2F_2?

(31) (*a*) Explain why a dilute solution of hydrogen chloride in water cannot be separated completely into its two components (water and hydrogen chloride) by boiling away the water. (*b*) Explain why a concentrated aqueous solution of hydrogen chloride cannot be completely separated into its components by evaporating away the hydrogen chloride.

(32) In what respects do the dry, gaseous or liquid, hydrogen halides differ from the aqueous solutions of the same substances?

(33) What are the characteristics of a strong acid?

(34) In what respects does hydrofluoric acid differ from the other corresponding compounds of the group?

(35) Make a tabular survey, similar to the one asked for in question (24), for the hydrogen compounds of the halogens. Include methods of preparation, and physical and chemical properties.

(36) What is the evidence that the constant boiling mixture of hydrogen chloride and water is not a compound of the two substances?

REFERENCES

Lowry—Historical Introduction to Chemistry, Chapter XII, gives a most interesting account of the discovery of the halogens and their compounds, as well as of their influence on the development of chemistry.

Alembic Club Reprints, Numbers 9 and 13. 9. The Elementary Nature of Chlorine, by Davy; 13. The Early History of Chlorine. Papers by Scheele (1774), Berthollet (1785), Morveau (1787), and Gay-Lussac and Thenard (1809).

Rogers—Industrial Chemistry, Chapter VIII, describes the manufacture of the elements; Chapter VI, the manufacture of hydrochloric acid.

G. Martin—Chlorine and Chlorine Products (1915). Chapter II describes briefly, but with many figures, various types of apparatus for the preparation of chlorine; Chapter III deals with liquid chlorine; Chapter VI with the manufacture of hydrochloric acid; Chapters VII and VIII with bromine and iodine; Chapter IX with hydrofluoric acid. Chapter I takes up the older processes for chlorine manufacture.

CHAPTER XII

CHEMICAL EQUILIBRIUM

Rule of Le Chatelier.—Dissociation of Gaseous Substances

Since reversible reactions will be encountered more and more frequently in the development of our subject, it is desirable to review and extend the study of such reactions before attempting to take up the problems raised at the close of the preceding chapter.[1]

The Law of Mass Action.—It has already been shown that the velocity of a given reaction at a definite temperature is proportional to the concentration of the reacting substances. The concentration is usually expressed in terms of the number of gram molecules per liter, and the velocity in terms of the change in concentration of the constituents in unit time. Assume that the reaction is one between 1 molecule of A and 1 molecule of B. The proportionality of velocity of reaction to concentration may then be expressed by the equation:

$$[A] \times [B] \times K_t = \text{velocity}$$

The terms $[A]$ and $[B]$ represent the concentration of each reactant at the time of measurement of the velocity, and K_t is a constant. The subscript, t, is used to indicate that the quantity K_t is constant only at constant temperature. K_t, furthermore, is constant only for a specific reaction, and is different for each reaction. Similar equations may be written for any other reactions. If C and D are the reacting substances, the equation becomes:

$$[C] \times [D] \times K'_t = \text{velocity}$$

[1] The student is advised to review the matter contained on pages: 82, 87 to 89, 99, 107 to 111, 120, 133, 135, 147.

K'_t is a constant, but has a different value from K_t. The statement concerning the proportionality of reaction velocity and concentration (with the corresponding equations) is called the **law of mass action.**[1]

The Law of Chemical Equilibrium.—Thus far nothing has been said about the nature of the products of the two reactions. Suppose that when A and B react they form C and D, and that when C and D react they form A and B, in other words, that the reaction is reversible. These assumptions do not alter in any way the factors affecting the velocity of either reaction, and the equations which have been written are still correct. In earlier discussions it has been pointed out that, in such reversible reactions, the velocities of reaction in the two directions must ultimately become equal to each other. At that point:

$$[A] \times [B] \times K_t = [C] \times [D] \times K'_t$$

The terms representing the concentration may vary; the K's are constants. Hence for convenience the equation may be written:

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{K_t}{K'_t} = K_{eq}$$

K_t and K'_t are constants, therefore their quotient is a constant, commonly called the equilibrium constant for the reaction. The equation just derived states that, at equilibrium, the product of the concentrations of the reaction products divided by the product of the concentrations of the reactants is a constant at a given temperature.[2] This statement, or the corresponding equation, is called the **law of chemical equilibrium.**

[1] When more than 1 molecule of A reacts with B the form of the law of mass action is slightly different. In general, when n molecules of A react with m molecules of B the law says that

$$C_A^n \times C_B^m \times K_t = \text{velocity}$$

[2] This equation is applicable to reactions in which only 1 molecule of each reacting substance appears in the chemical equation. For a reaction of the type $nA + mB \rightarrow pC + qD$ the law of chemical equilibrium reads:

$$\frac{[C]^p \times [D]^q}{[A]^n \times [B]^m} = K_{eq}$$

Suppose that after the reaction has attained equilibrium, more of the substance C is added to the mixture. Since this change increases the concentration of C, the fraction can no longer be equal to K_{eq}, and the system is no longer at equilibrium. In order that equilibrium may be regained, the concentrations of the reacting substances must change in such a way that the value of the fraction decreases. This can occur only by the removal of the added material, and the only way in which C can be removed is by reacting with D. Hence the concentration of D must decrease, some of the added C must be used up, and A and B must increase in amount. Thus the fraction grows smaller until equilibrium is restored. In the same way removal of C or D causes more of A and of B to react with each other in order to replace the material taken away. The equation developed allows the exact conditions under which equilibrium is attained from a mixture of any concentration to be calculated if the equilibrium constant is known. In this text, such calculations will not be undertaken; the student should use the equations to make sure that he can predict the effect of any change in concentration in a system at equilibrium.[1]

The Rule of Le Chatelier.—The equation just discussed deals only with the influence of concentration in reversible reactions, and gives no information about the influence of temperature or of pressure, except in those cases in which the concentration of the reacting substances is directly proportional to the pressure. Exact equations relating these various factors are too complex for this text. But there is a very simple rule which permits the effect produced by any change in a system at equilibrium to be determined qualitatively. The **rule of Le Chatelier** states that **if a system at equilibrium is subjected to any stress, a change which reduces the stress will occur.** Since the term " stress " is used very broadly in this rule, a number of illustrations of its application will be taken up.

(1) When to a system in equilibrium, an **additional amount of any component** is added, the additional quantity is a " stress." The system will change so as to remove the additional amount.

[1] An excellent series of applications of the equation will be found in Stieglitz, Qualitative Analysis, Vol. I.

This can occur only by reaction of the added material. Thus in the reaction $A + B \rightleftarrows C + D$, addition of A causes reaction in the direction that removes A, and so on. This conclusion has already been reached by studying the equation for the equilibrium constant. A second application of the same sort concerns the **removal of a component.** The deficiency in the amount of this component is a "stress"; the reaction will proceed to replace the component. Practical applications have already been encountered. Thus it was pointed out that when chlorides are to be oxidized by agents the oxidizing strength of which is of the same order as that of chlorine, an excess of the oxidizing agent must be used. Another illustration is the reaction between sulfuric acid and sodium chloride which goes to completion only when the hydrogen chloride is removed as fast as it is formed. Similar is the case of the equilibrium between chlorine and water—only a little chlorine can react with water to give hypochlorous acid before equilibrium is attained. Nevertheless the chlorine ultimately reacts completely with the water, because the hypochlorous acid formed decomposes into hydrochloric acid and oxygen, which escapes from the solution. The formation of precipitates is another method of causing reactions to proceed to completion, because the precipitated material is removed from the field of action. This removal constitutes the "stress" and the reaction proceeds so as to replace the precipitated component.

(2) **When pressure is applied to a system in equilibrium,** the applied pressure constitutes the stress. In gaseous systems the pressure is proportional to the number of molecules. A gaseous system to which pressure is applied can, therefore, relieve itself of the stress only if the reaction proceeds in the direction which causes a decrease in the number of molecules. In the reaction:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

the number of molecules decreases from 4 to 2 as reaction proceeds to the right. Increase of pressure on the system therefore drives the action to the right, decrease of pressure has the reverse effect. On the other hand, in the reaction $H_2 + Cl_2 \leftrightarrows 2HCl$, 2 molecules give rise to 2 new molecules; no change in number

of molecules accompanies the reaction. Consequently, there is no way in which this system can adapt itself to changes in external pressure, and such changes are therefore without effect.

Before proceeding to other illustrations, one important point must be recalled. The relationship between number of molecules and pressure exists only in the case of gases, and the rule cannot be applied to pressure effects in solid or liquid systems unless the volume changes occurring in the reaction are known. This is rarely the case. But when the system contains both solids or liquids and gases, the rule may be applied. Take for example the reaction:

$$Fe_3O_4 + 4H_2 \leftrightarrows 3Fe + 4H_2O$$

Both iron and its magnetic oxide are solids, and the volume of the solid is so small in comparison to the volume of the gaseous substances that it may be neglected entirely. At the temperature of the reaction, water is in the form of vapor. Hence, there is no appreciable volume change in this reaction, for 4 molecules of one gaseous substance give rise to 4 molecules of another. Pressure, therefore, has no influence on the reaction.

Another illustration is the effect of increase of pressure on the freezing point of water. Water at 0° has a greater density than ice at this temperature; that is the process of melting is accompanied by contraction in volume. If, therefore, a mixture of ice and water at 0° is placed in a vessel of such construction that pressure can be applied to the mixture without changing the temperature, the ice will melt under pressure because the resulting contraction causes a decrease of pressure. The student will be able to visualize this effect by imagining a cylinder and piston for carrying out the experiment. Since, as has just been shown, water is liquid at 0° under increased pressure, further cooling is required to solidify it again—in other words, the freezing point of water is lowered by increase of pressure.[1] Most sub-

[1] At very high pressures (several thousand atmospheres) a solid of crystalline form different from that of ordinary ice is formed. This modification of solid water is more dense than liquid water, and consequently these very high pressures cause a rise of freezing point. At 20,000 atmospheres pressure, for example, the freezing point of water is + 78° C.

stances, however, contract on freezing, and rise in pressure, therefore, usually raises the freezing point. In all cases, the effects of pressure changes on the freezing point are very minute, because the volume changes accompanying the transition from liquid to solid and *vice versa* are very small. A pressure of approximately 100 atmospheres is required to lower the freezing point of water by 1°.

(3) **Influence of temperature.**—Temperature changes are brought about by conducting heat into a system or away from it. The gain or loss in heat constitutes the "stress," and the system adapts itself to the stress by either absorbing heat or giving it out. In the formation of ammonia from hydrogen and nitrogen heat is liberated, as may be shown by writing the equation:

$$3H_2 + N_2 \rightleftarrows 2NH_3 + \text{heat}$$

When the temperature is raised, the system tends to use up the added heat, and the reaction proceeds to the left. Lowering the temperature, on the other hand, shifts the equilibrium to the right.[1] The reaction is discussed further in Chapter XXI. The effect of temperature is just the opposite in the reaction:

$$2NO \rightleftarrows N_2 + O_2 + \text{heat}$$

In this case, rise of temperature causes the reaction to go to the left in order to use up the added heat. But reaction to the left (as the equation is written) means formation and not decomposition of the compound. Of course, the terms "to the left" and "to the right" are arbitrary, since equations for reversible reactions may be written with either pair of reactants on the left or right side.

The rule may be used to determine the effect of temperature upon solubility. Solubility is a statement of the quantity of dissolved material contained in a saturated solution, that is, in a solution at equilibrium. If heat is given out during the

[1] From what has just been said and from the discussion of the influence of pressure on the equilibrium in the case of this reaction, it can be understood why, when ammonia is to be prepared from its elements, as high a pressure and as low a temperature as possible are employed.

process of dissolving, the equilibrium in question may be represented by the equation:[1]

$$\text{solute} \rightleftarrows \text{solution} + \text{heat}$$

According to Le Chatelier's rule, rise of temperature must drive the reaction to the left so that the heat introduced into the system may be removed. Lowering of temperature obviously must have the opposite effect. If, on the other hand, heat is absorbed during the process of dissolving, the temperature effects must be exactly the reverse of those just described. In other words, a substance which dissolves with evolution of heat is less soluble at high temperatures than at low ones, and *vice versa*. But this rule must be used cautiously. When a substance is dissolved in a relatively large amount of water, two changes occur. In the first place, the solute is dissolved; in the second, the solution is diluted. Hence, the total heat effect is really the sum of the heat of solution and the heat of dilution. In judging of the effect of temperature on solubility, only the former is to be considered. This quantity can be determined most readily by dissolving the solute in an almost saturated solution of the solute; under these conditions practically no dilution can occur after the material dissolves, and the heat effect observed is the actual heat of solution.

The student is urged to become familiar with the use of Le Chatelier's rule by applying the principle to as many reactions as he can. To aid him in this, a number of cases are taken up in the problems at the close of this chapter. In making these applications, two common errors should be avoided. In the first place, the principle under discussion is applicable only to reversible reactions. In the second place, a necessary condition for reversibility is that all of the substances involved be in the same vessel. Students commonly make the error of thinking that pressure or heat can be applied "to the right-hand side (or left-hand side) of the reaction." In thinking this, they are confusing the reaction and the equation. In the reaction all of the

[1] In order to avoid confusion, the equation has been written without the solvent, since the change is not a chemical change in the ordinary sense.

substances are intermingled, and heat or pressure cannot be applied to any individual ones or any pair of substances. Finally each of the effects should be considered by itself. When pressure changes are considered, the temperature should be thought of as constant, and *vice versa*.

Energy and Chemical Change

In the preceding discussion and in many others throughout the text, the heat developed or absorbed during the course of a reaction has been mentioned. It is manifest that changes in heat content usually accompany chemical changes. As a matter of fact, many reactions are carried out in practice in order to profit by the energy changes rather than to accomplish specific chemical results. In the burning of fuels the heat or power produced are the important results, and the chemical change is merely the means to the end.

Heat is, however, only one form of energy, and if heat is liberated in reactions or used up by them, chemical changes should produce or be brought about by other forms of energy. The use of electricity has already been encountered in the electrolytic preparation of chlorine. All batteries are illustrations of the production of electrical energy by chemical means. (See Chapter XXXVIII.) Light is often produced by reactions, independent of the temperature at which the reaction is taking place, and light may likewise cause chemical changes. For instance, the production of light by fireflies seems to be a chemical reaction in which very little heat is produced. The reactions in a photographic film are chemical changes brought about by the influence of light. Chemical reactions may be made to do work when they are accompanied by changes in volume. This is illustrated by the action of explosives, either in propelling projectiles through the air or in driving internal combustion engines.

It was at one time thought that the amount of heat liberated in a reaction is a measure of the "affinity" of the reacting components for one another. Although the amount of heat liberated is often an approximate measure of the tendency of two

substances to react with one another, it is not the only factor to be considered. Otherwise, since heat is liberated only when the reaction proceeds in one direction, it might be concluded that the opposite reaction is impossible, whereas it is well known that this is not the case. The relationship between the heat of reaction and chemical affinity or activity cannot here be discussed; the subject is treated adequately only in text books of thermodynamics.

It was pointed out in an earlier discussion that the amount of heat liberated or absorbed in a given chemical reaction depends practically only on the quantity of reacting materials. The heat of reaction varies slightly with the temperature at which the reaction is carried out, but the variation is so small that it usually possesses no practical importance. The heat of reaction for different chemical changes, however, varies greatly—in some cases it is so small that it is hardly noticeable while in others it may be enormous. The value of coal as a fuel is due to the fact that in the reaction between carbon and oxygen a relatively large amount of heat is given out. Only one type of reaction produces no heat effects whatsoever.

Heats of reaction may sometimes be calculated in a very simple way when the heats of reaction of related chemical changes are known. Thus carbon may react with oxygen to form carbon monoxide. The reaction is rather difficult to control as the carbon monoxide readily reacts with more oxygen to form carbon dioxide. Hence, it is rather difficult to measure the heat of reaction of the first action. But the heat of the reaction between carbon monoxide and oxygen is known, and the heat of the reaction between carbon and oxygen to form carbon dioxide directly has also been measured. The facts may be put into the equations:

$$2CO + O_2 \rightarrow 2CO_2 + 136{,}400 \text{ cals.}$$

and

$$2C + 2O_2 \rightarrow 2CO_2 + 193{,}640 \text{ cals.}$$

in which the number at the end of each equation represent the calories of heat liberated when the quantities of carbon monoxide and of carbon indicated in the equations are burned. The amount of heat liberated in the reaction:

$$2C + O_2 \rightarrow 2CO$$

is the difference between the two amounts given above, 57,240 cals. According to the equation, this amount of heat is given out when 24 grams of carbon burn to carbon monoxide—the heat of reaction is usually stated in terms of gram molecules of material. In this case it would be one-half of 57,240 cals. This illustration represents a type of calculation very useful for finding heats of reaction when direct measurement is difficult. Other methods of calculating heats of reaction from fundamental properties of the atoms cannot here be taken up.

Dissociation of Gases

In many cases the molecular weight of a gaseous substance apparently fails to agree with the analytical data. An illustration of this is the case of phosphorus pentachloride. Analysis shows that in 100 grams of the substance there are 85.1 grams of chlorine and 14.9 grams of phosphorus. To obtain the formula each number is divided by the corresponding atomic weight. $85.1 \div 35.46 = 2.4$ and $14.9 \div 31.04 = 0.48$. The first quotient is evidently five times the last, and the formula is therefore either PCl_5, or P_2Cl_{10}, or P_xCl_{5x}. The substance is a solid at ordinary temperatures but can be volatilized by heat. Its weight in gaseous form per 22.4 liters at some elevated temperature may therefore be determined, and the data recalculated for 0° C. by the gas laws. Before examining the actual data, the results which might be obtained on the assumption that one or the other of the preceding formulae is correct may be calculated. If the formula is PCl_5, the weight of 22.4 liters of the gaseous substance at 0°, 760 mm. should be 208.3 grams. At 300° the weight of the same volume of gas would be less, since the density of a gas decreases with rise in temperature. From the gas laws, the weight at 300° should be:

$$208.3 \times \left(\frac{273}{273 + 300}\right) = 99.25 \text{ grams}$$

If the formula is P_2Cl_{10} the weight should be twice as great, and, in general, if the formula is P_xCl_{5x} the weight of 22.4 liters should be x times 99.25 grams at 300° C., 760 mm. As long as the atomic weights (31.04 for phosphorus and 35.46 for chlorine)

as well as the analytical data are accepted, the weight, 99.25 grams, is obviously the smallest possible weight for 22.4 liters of the substance under the conditions stated. The weight actually obtained is, however, only about one-half of 99.25 grams. Since the quantity of a gaseous substance contained in 22.4 liters is the gram molecular weight, the facts may be stated as follows: "the molecular weight of phosphorus pentachloride experimentally obtained is smaller than the smallest molecular weight that can be calculated from the analytical data on the basis of the generally accepted atomic weights."

Another and a very useful way of describing this phenomenon is the following. If the formula of the substance is PCl_5, 208.3 grams of the vapor, contained in a volume of 22.4 liters at 0°, should exert a pressure of 1 atmosphere. At 300° the pressure should be $1 \times \frac{273 + 300}{273} = 2.1$ atm., approximately. If the formula is P_2Cl_{10}, 208.3 grams represents only one-half of a molecular weight, and the pressure should be only one-half as great. If the formula is P_xCl_{5x}, 208.3 grams is only $1/x$ of a molecular weight, and the pressure at 300° should be only $2.1/x$ atmospheres. On the basis of any of the possible formulae of phosphorus pentachloride, 2.1 atmospheres is obviously the largest pressure that 208.3 grams of the substance could produce if vaporized into 22.4 liters at 300°. Actually, however, the pressure found by experiment is approximately twice 2.1 atmospheres. The substance therefore exerts twice the largest pressure expected from its chemical composition and the accepted values for the atomic weights of its constituent elements.[1]

For a long time phenomena of this type stood in the way of general acceptance of Avogadro's law which, of course, underlies all of the calculations made above. But when viewed correctly, the phenomenon is one of the strongest supports of the law. On the basis of Avogadro's law, the facts summarized in the last statement of the preceding paragraph must mean that there are more molecules present in the vapor than can be accounted for

[1] The calculations have been made on the assumption that the vapor of phosphorus pentachloride obeys the gas laws. While this is not strictly correct, the deviations would not materially alter the conclusions.

on the assumption of the formula PCl_5. The only way in which the formation of more molecules than correspond to this formula can be explained, without contradicting the analytical data or the results of atomic weight determinations, is by assuming that in the process of vaporization the molecules of PCl_5 decompose into a larger number of lighter molecules, for example, into PCl_3 and Cl_2. If this decomposition were complete, the pressure exerted by the vapor would be twice as great as that calculated on the basis of the formula PCl_5, since there would be twice as many molecules as in the undecomposed material. The molecular weight of the vapor would be the average of the molecular weight of phosphorus trichloride and chlorine, or $(137.32 + 70.92)/2$, which is one-half the molecular weight of phosphorus pentachloride. The calculations made on the assumption of complete decomposition of phosphorus pentachloride into the substances named, agree with the density and pressure data actually found. Nevertheless this deduction would not have been accepted by chemists if it had not been shown that the vapor of phosphorus pentachloride behaves chemically like a mixture of chlorine and the trichloride of phosphorus. Chlorine is appreciably less dense than the trichloride. Consequently, the latter should diffuse more slowly than the former. When the pentachloride is volatilized in a tube, one end of which is closed by an asbestos plug, free chlorine first diffuses out through the plug.[1]

The behavior of phosphorus pentachloride is typical of the behavior of many other substances; moreover it is similar to that of a most important class of solutions. The conclusions drawn may be summarized in the following statement. **Whenever a substance has a smaller molecular weight than the smallest to be expected on the basis of its chemical composition and the**

[1] Experimental evidence of similar dissociation may easily be shown in the case of two other substances which behave like phosphorus pentachloride, namely phosphorus pentabromide and ammonium chloride. In the former the color of the bromine liberated is an indication of dissociation; in the latter, the more rapid diffusion of the ammonia liberated may be demonstrated by heating the ammonium chloride in a glass tube. Moist litmus held at the mouth of the tube first turns blue on account of the action of ammonia, and later turns red because of the action of the hydrogen chloride which diffuses more slowly.

accepted atomic weights of its constituents, or whenever it exerts a greater pressure than is to be expected on the same basis, the substance is likely to have suffered dissociation. Before dissociation may be assumed with certainty, the chemist must demonstrate that the chemical behavior of the substance is in complete accord with this assumption.

Dissociations like that of phosphorus pentachloride are reversible reactions, and are therefore subject to the influences discussed in earlier sections of this chapter. For the case of phosphorus pentachloride, the equation for the dissociation is:

$$\text{Heat} + PCl_5 \rightleftarrows Cl_2 + PCl_3$$

Rise of temperature should therefore increase dissociation, while rise in pressure, or addition of an excess of the trichloride or of chlorine, should decrease the extent of decomposition. It has already been mentioned that in order to prepare the pentachloride an excess of chlorine must be used, and the reason for this experimental fact is now clear. The following facts show that the influence of temperature is the one postulated. At temperatures lower than 300° the vapor of the pentachloride exerts a greater pressure than that expected on the basis of the formula PCl_5, but the pressure is not twice as great as the expected value. Another way of putting the same thing is to say that the molecular weight of gaseous phosphorus pentachloride, at temperatures below 300°, is less than that corresponding to the formula, but is more than one-half the expected value. These facts mean that some, but not all, of the molecules have decomposed. Lowering of the temperature, then, decreases dissociation since the data for 300° indicate nearly complete dissociation. This is in accord with Le Chatelier's rule.[1]

[1] The various effects upon the equilibrium may be simply demonstrated with the substance PCl_3Br_2, which dissociates into PCl_3 and Br_2. Equivalent amounts of PCl_3 and Br_2 are placed in two heavy glass tubes which are then sealed. A third tube containing an excess of PCl_3 is prepared. The first two tubes are placed in beakers containing water at different temperatures, say 35° and 50°. The tube immersed in the cooler water shows much less color, indicating the presence of less free bromine. When the tube containing the excess of PCl_3 is placed next to the other tube in the warmer water, it is found to have less color.

EXERCISES

(1) Suppose substances A and B react with each other at constant temperature. What happens to the concentration of the two substances and what, therefore, to the rate of the reaction?

(2) Suppose the substances A and B have just been mixed. The two are to react with each other to form C and D. C and D, in turn, are supposed to react with each other to form A and B. (*a*) What must be the relative rate of reaction between A and B on the one hand, and between C and D on the other hand, at the moment of mixing of A and B? (*b*) What happens to the concentrations of A and of B, and what to the concentrations of C and of D? (*c*) What must therefore happen to the rates of the two opposing reactions immediately after mixing? (*d*) To what state of affairs must these changes in rates ultimately lead?

(3) Suppose the reaction $A + B \rightleftarrows C + D$ has come to equilibrium. (*a*) What does that statement mean with respect to the velocities of the two opposing reactions? (*b*) Which reaction will be **directly** affected by removal of some of the substance B, and how? (*c*) Immediately after the removal of some of B, will the two rates of reaction still be the same? If not, which one will be the faster? (*d*) What must be the effect of these changes upon the concentrations of the other substances involved? (*e*) What will be the final effect of the removal of B?

(4) What would be the effects of (*a*) removal of C, and (*b*) addition of more A? Answer as in (3), (*b*), (*c*), (*d*), and (*e*).

(5) State Le Chatelier's rule.

(6) Apply Le Chatelier's rule to a discussion of the effect of adding an excess of chlorine to the equilibrium mixture represented by the equation:

$$PCl_3 + Cl_2 \rightleftarrows PCl_5$$

Explain in detail how the conclusion is reached by application of the rule. Always write the equation for the reaction before starting a discussion of this sort.

(7) Suggest methods for causing the following reaction to go further toward the right without changing the temperature of the reaction mixture:

$$2HI \rightleftarrows H_2 + I_2$$

Assume that the temperature is sufficiently high to keep all of the reacting substances in the gaseous condition.

(8) Discuss in detail, from the point of view of Le Chatelier's rule the

effect of (*a*) rise of temperature and (*b*) decrease in pressure, on the equilibrium in each of the following cases:

(1) Heat + $2NH_3 \rightleftarrows N_2 + 3H_2$
(2) $2NO + O_2 \rightleftarrows 2NO_2$ + heat
(3) $N_2 + O_2$ + heat $\rightleftarrows 2NO$

(9) What effect does dilution with an indifferent gas have on the equilibrium:

$$2SO_2 + O_2 \rightleftarrows 2SO_3?$$

(10) At about 300° C. what effect does increase of pressure have on the equilibrium: $H_2S \rightleftarrows H_2 + S$? Note that at this temperature sulfur is practically completely in the liquid state.

(11) In general do substances which are more soluble at high temperatures than at low ones, dissolve with evolution or with absorption of heat? Answer from the point of view of Le Chatelier's rule.

(12) What must be true of the heat effect accompanying solution of substances which are less soluble at higher than at lower temperatures?

(13) If a reaction is driven more nearly to completion by rise in temperature, what may be said of the heat effect accompanying the reaction?

(14) Explain the effect of increase of pressure on the melting point of ice.

(15) Molten copper has a larger volume per gram of material than solid copper. How is the melting point of the element affected by increase of pressure? Is the effect large? Why?

(16) A compound consists of 7.2 per cent of phosphorus and 92.8 per cent of bromine. (*a*) What formulae agree with these data? (*b*) Calculate from the simplest formula what pressure should be exerted by 430.64 grams of the substance if volatilized in a space of 22.4 liters at 300° C. (*Ans.* 2.9 atmospheres, approximately.) (*c*) Calculate what pressure should be exerted by the same weight of material if the most complex formula is the correct one. (*d*) If the actual pressure had been 4.35 atmospheres, what conclusions might be drawn from the calculations and the facts?

(17) A solid substance consists of 59.9 per cent of oxygen and 40.07 per cent of sulfur. (*a*) From these data what formulae might be obtained for the substance? (*b*) What would the molecular weights of the substance be according to the various formulae possible according to the analytical data? (*c*) Determinations of the molecular weight made by volatilizing the substance at high temperatures lead to the value 53+. What conclusion may be drawn from this fact? (*d*) Describe briefly

the experimental data involved in the statement that the molecular weight of the gaseous substance at a high temperature, say at 900°, is 53+.

REFERENCES

HILDEBRAND—Principles of Chemistry, Chapter XII.

CARTLEDGE—Inorganic Physical Chemistry, pages 191–202, and 207–212. Both of these references contain simple treatments of chemical equilibrium.

MILLARD—Physical Chemistry for Colleges, Chapter VII, contains interesting data on thermochemistry. Methods of measurement of heat effects are described and data are given.

CHAPTER XIII

THE THEORY OF IONIZATION, I

Experimental Basis.—Electrolysis.—Faraday's Law.—Degree of Ionization of Electrolytes

The methods described in Chapter X for determining molecular weights of substances in solution yield results which agree well in a very large number of cases with the composition and the chemical behavior of the substances. But many other substances, when dissolved in certain types of solvents, behave very much like the gaseous compounds discussed in the preceding section on dissociation—that is, the experimentally determined molecular weights are smaller than the smallest calculable value. The compounds which exhibit this behavior are salts, acids, and bases.

Aqueous solutions of hydrogen chloride are an excellent illustration of the phenomenon just described. The composition of this substance indicates the formula H_xCl_x, and 22.4 liters of it at 0°, 760 mm. weigh approximately 36.5 grams, indicating that x in the formula is 1. The molecular weight of hydrogen chloride, when determined by the freezing-point method, is, however, far less than 36.5. In very dilute solutions the molecular weight approximates one-half of the value obtained in the gaseous state, and, although it seems to increase somewhat when the solution is concentrated, it never even approaches the value required for the formula, HCl. Another illustration is the salt, sodium chloride. It is not volatile enough to permit the determination of the weight of 22.4 liters in the gaseous condition. But it is composed of 60.65 per cent of chlorine and 39.35 per cent of sodium. $60.65 \div 35.46 = 1.711$ and $39.35 \div 23.0 = 1.711$. Hence, the formula is Na_xCl_x, and the smallest molecular weight corresponding to this type of formula is 58.46.

The molecular weight of sodium chloride, when determined in dilute aqueous solution by any one of the three methods described, is about one-half of the expected value. In other cases the molecular weight in dilute solutions approaches values which deviate even more from the ones calculated from analytical data. The observed molecular weight of sulfuric acid, as the solution is diluted, approaches a value only one-third of that calculated.

In the discussion of the analogous phenomenon among gaseous substances, it was concluded that substances which exhibit a molecular weight smaller than the smallest one expected are probably dissociated. But it was emphasized that this assumption should never be made unless the material possesses the chemical properties characteristic of a mixture such as would result from dissociation. The same precaution should be shown in accepting dissociation as the cause of the low molecular weights of substances in solution. What products, for example, may be assumed if hydrogen chloride dissociates? Since the compound is composed of hydrogen and chlorine only, dissociation could seemingly lead only to the formation of hydrogen atoms and chlorine atoms. The most characteristic property of hydrogen atoms is that they tend to unite with each other to form hydrogen molecules; the corresponding reaction takes place with chlorine atoms. But there are two obvious objections to the assumption that dissociation leads to the formation of these 2 atoms in aqueous solutions. If molecular hydrogen and molecular chlorine were the final products, the reaction would be:

$$2HCl \rightarrow H_2 + Cl_2$$

Neither the number of molecules nor the total weight of material is changed by the reaction. Consequently, the apparent molecular weight of an equimolecular mixture of hydrogen and of chlorine would be the same as that of hydrogen chloride. In the second place the properties of hydrogen and chlorine are so different from those of a solution of hydrogen chloride that it is utterly impossible to assume that the latter gives rise to these two elements in solution. Thus, neither hydrogen nor chlorine is very soluble in water; hydrogen chloride on the other hand is

very soluble, and no evolution of gas occurs from the solution. Chlorine is a powerful oxidizing agent and has a strong odor—dilute hydrochloric acid is a reducing agent and has no odor. Similarly sodium chloride is composed of sodium and chlorine only, and dissociation, so far as the facts presented enable us to judge, should result in the formation of these elements. The properties of chlorine are not at all like those of the relatively inactive, colorless, odorless sodium chloride. Sodium, we know, acts violently with water to form hydrogen—no reaction of this sort occurs when sodium chloride is dissolved in water.

All acids, bases and salts behave, so far as their molecular weights in aqueous and similar solutions are concerned, like hydrogen chloride and sodium chloride. But in all cases, the products of dissociation postulated without further knowledge of the characteristic behavior of such solutions, possess properties which are not in accord with the actual properties of the solutions. This discussion may therefore be summarized by saying that, **although molecular weight determinations for acids, bases and salts in aqueous and in similar solutions suggest the likelihood of dissociation, this suggestion cannot be accepted until further study of such solutions has led to the discovery of products of dissociation, the properties of which are those of the solutions.**

Electrolytes.—Pure water and all other common non-metallic solvents are very poor conductors of electricity. The conductivity of the purest water thus far prepared is approximately $\frac{1}{25,000,000}$ of that of mercury. Slight impurities greatly increase the conductivity; ordinary distilled water conducts about 250 times as well as the specially pure sample mentioned. Certain classes of solutions also are very poor conductors, but solutions of **acids, bases** and **salts** in water or similar solvents are good conductors. Two points must be emphasized—in order to make a solution which is a good conductor of electricity it is necessary to choose not only a suitable solute but also a suitable solvent. The first of these points is illustrated by the fact that aqueous solutions of sugar, alcohol, or other substances, not acids, bases, or salts, are as poor or even poorer conductors than water itself; but aqueous solutions of hydrogen chloride and similar substances

have high conductivities. The second point is illustrated by the fact that although the solution of hydrogen chloride in water is a good conductor, a solution of the same substance in toluene or benzene is not. Substances which produce conducting solutions in certain solvents are called **electrolytes.**[1]

Phenomena Accompanying the Passage of Electricity through Solutions of Electrolytes.—The passage of a current of electricity through a metal produces no visible changes. The passage of electricity through a solution, on the other hand, is accompanied by **two** important phenomena. In the first place, chemical changes occur at the electrodes. The reaction which occurs at the positive pole is different from the one which goes on at the negative pole. In the second place, matter is transported through the solution. Two illustrations will be cited. When an aqueous solution of hydrogen chloride is subjected to **electrolysis** (as the passing of an electrical current through a solution is called), hydrogen is liberated at the negative pole, or **cathode,** and chlorine at the positive pole, or **anode.**[2] At the same time changes in the concentration of the solution around the **electrodes** (poles) indicate that hydrogen is transported toward the negative pole away from the positive pole, while chlorine is transported in the opposite direction.

Another illustration is electrolysis of a solution of copper permanganate.[3] The solution is placed in a U-tube so as not to fill the arms of the tube completely. Above the solution a layer of dilute nitric acid is carefully poured into each arm, in such a way that the nitric acid and the colored solution do not mix appreciably. One platinum electrode is then introduced into the nitric acid in one arm, another electrode into the acid in the other arm, and the current passed through the solution. After a few minutes a blue zone of color appears at the lower portion of the nitric acid on the negative side, and a pinkish zone

[1] Since electrolytes are substances which furnish ions, they are also called **ionogens.**

[2] From very dilute solutions of hydrochloric acid, oxygen is obtained at the positive pole. In the experiment platinum electrodes should be used.

[3] A solution for use in this experiment can be conveniently prepared by mixing aqueous solutions of potassium permanganate and of copper nitrate.

in the nitric acid on the positive side. The bluish material travels through the nitric acid to the negative pole, and is there changed to a reddish deposit on the electrode; the pinkish substance travels to the other electrode, and there either disappears or, depending on the concentrations and voltage, produces a black material. All copper salts in dilute aqueous solution have a bluish color; this fact and the deposition of the red substance (which can easily be shown to be finely divided copper) show that a substance containing copper must have traveled through the solution toward the negative pole of the circuit. On the other hand, permanganates in dilute aqueous solution have a pinkish color and it may therefore be concluded that some constituent of permanganates has traveled through the solution in the opposite direction.

These two illustrations are typical of the phenomena which occur whenever a current is passed through any conducting solution; other instances and the details of the chemical changes will be taken up later. For the present it should be borne in mind that **the passage of electricity through a solution is always accompanied (1) by transport of matter in which one kind of matter is carried toward the positive and a different kind toward the negative pole, and (2) by chemical changes at the electrodes, in which one or more substances are produced at one pole and different substances at the other pole.**

Interpretation of the Phenomena of Electrolysis.—The attraction of matter toward a charged pole is no new experience for any one familiar with even the most elementary facts of electricity. A positively charged body attracts negatively charged particles and *vice versa*. This at once suggests that solutions of electrolytes contain positively and negatively charged molecules, and that the positively charged ones travel toward the negative pole, and the negatively charged ones to the positive pole. When they reach the poles, they become discharged, as would any charged body which comes into contact with another body carrying an opposite charge. When discharged, they undergo a change in chemical character. This latter statement must receive further amplification before it can be fully accepted, and will be treated more fully in another section of this chapter. The

hypothetical, positively charged substances are called positive ions, or **cations** because they travel to the cathode (negative pole); and the negatively charged substances, negative ions, or **anions** because they travel to the anode (positive pole).

The phenomena of electrolysis therefore suggest that solutions of electrolytes contain positive and negative ions, but, **taken by themselves, these phenomena tell nothing about the origin, the relative weight, or the chemical properties of these ions.**

Connection between the Molecular Weights of Electrolytes in Solution and the Phenomena of Electrolysis.—The *significant* fact about the phenomena described is that only those solutions in which the solutes exhibit an unexpectedly small molecular weight are conductors of electricity. Thus pure hydrogen chloride, whether in the gaseous form or as a liquid, is a non-conductor. A solution of hydrogen chloride in toluene or in benzene is likewise unable to carry the current. In all of these forms hydrogen chloride has a molecular weight fully in accord with its percentage composition. Aqueous solutions of hydrogen chloride, on the other hand, are excellent conductors, and in these solutions the molecular weight of the solute is approximately one-half of that expected. What is true of hydrogen chloride is true of all electrolytes. Every non-metallic solution which is a conductor of electricity contains some substance which, in that solution, exhibits a molecular weight smaller than the one calculated from its percentage composition; every solution which contains substances of molecular weight smaller than anticipated, is a conductor.[1] This extraordinary parallelism almost necessitates the very simple conclusion that these **conducting solutions contain charged particles produced by the dissociation of the molecules of the electrolyte.**

Origin of the Charges on the Ions. Chemical Character of the Ions.—When the facts about the molecular weights of electrolytes in aqueous solution were presented, it was pointed out that the assumption of dissociation could not be accepted until the discovery of dissociation products with properties in accord with those of the solution. The low molecular weight of hydrogen

[1] There are a few exceptions to this statement, but they seem to be of no significance.

chloride in aqueous solution, for example, could not be explained by assuming dissociation into hydrogen and chlorine atoms, because the chemical evidence does not agree with this interpretation. According to the conclusions of the preceding paragraph, it might be said that, in aqueous solution, hydrogen chloride dissociates into positively charged hydrogen, or hydrogen ion (H^+), and negatively charged chloride ion, (Cl^-). This assumption is an improvement over the first one only if these ions are supposed to have chemical properties entirely different from those of the uncharged atoms or molecules which they resemble in formula. That this assumption is not unwarranted will become clear when the origin of the charges on the ions is understood.

According to modern theories, atoms consist of a positively charged nucleus and an outer shell or layer of (negatively charged) electrons. In the neutral atom, the number of electrons is just equal to the number of positive charges on the nucleus, so that the atom as a whole has no net charge. Suppose that such an atom should lose one of its electrons from the "shell," or outer layer. There would then be one more positive charge on the nucleus than there are electrons surrounding it, and the atom would consequently possess a net positive charge of 1 unit of electricity. If 2 electrons were lost, the net positive charge would be 2, and so on. In this way, the positive ions may be imagined to be formed. But the electrons thus lost by the atoms transformed into positive ions must go somewhere; the simplest assumption is that they attach themselves to other atoms. If the atoms to which these electrons become attached were originally neutral, they must become negatively charged by gaining the extra electrons. For each electron they gain, they acquire 1 unit of electricity. According to this hypothesis, the process of dissociation of hydrogen chloride into ions consists simply of the transfer of 1 electron from the hydrogen atom to the chlorine atom.

The point of view just outlined carries with it many implications, which will be further discussed below; one of these is particularly pertinent at this phase of the discussion. According to the electron theory of matter (see page 44), the chemical properties of the atoms are determined by the number and the

arrangement of the electrons around the nucleus. Therefore if, in the process of ionization, the atoms lose or gain electrons, the properties of the resulting substances must be different from those of the original atoms. The process of ionization is, in other words, a chemical change, and the ions are the products of this reaction.

Theory of Ionization.—What has been thus far described may be summarized as follows. Certain substances in certain solvents are dissociated into positively and negatively charged molecules, called ions, which possess independent chemical characteristics. This theory was first presented by Arrhenius, and is called the **theory of ionization.** Two other important points should be added to the statement. Since solutions, even though they are ionized and contain charged particles, never have any apparent net charge, molecules must ionize in such a way that the number of positive charges on the positive ions is exactly equal to the number of negative charges on the negative ions. It is further assumed that electrolytes become more and more dissociated as the solution is diluted until finally (at a point called infinite dilution) dissociation into ions is complete. This hypothesis will be discussed under the heading "Degree of Dissociation of Electrolytes."

Faraday's Law. Valence and the Theory of Ionization.—From many solutions—such as aqueous solutions of all acids, most bases and many salts—hydrogen is liberated at the negative pole. Irrespective of the nature of the solution, the temperature, the pressure or any other influences, the quantity of electricity required to liberate a given weight of hydrogen is always the same. For the gram atomic weight, 1.008 grams, 96,500 coulombs [1] of electricity must pass through the solution. This same quantity of electricity deposits 1 gram atomic weight of silver (107.88 grams) at the cathode. In order, however, to deposit 1 gram atomic weight of copper from a solution of copper

[1] One coulomb is the quantity of electricity which flows through the circuit when a current of 1 ampère flows for 1 second. The amount of hydrogen liberated by 96,500 coulombs is 1 gram atomic weight, provided that no other product is formed at the same electrode, and that no reaction which uses up the hydrogen occurs.

sulfate, $2 \times 96{,}500$ coulombs are necessary. To obtain 1 gram atomic weight of iron by electrolytic deposition from a solution of ferrous sulfate, $2 \times 96{,}500$ coulombs are also required. But to obtain the same quantity of iron from a solution of ferric sulfate, $3 \times 96{,}500$ coulombs are necessary. Hydrogen and silver are univalent elements, copper is bivalent, iron in ferrous sulfate is also bivalent, but iron in ferric sulfate is trivalent. Evidently the quantity of an element deposited at an electrode by 96,500 coulombs, is its gram atomic weight divided by its valence in the compound from which it is liberated. This quantity is the gram equivalent weight. It may therefore be stated that "equal quantities of electricity liberate or deposit equivalent quantities of the elements." This statement is called **Faraday's law,** and the quantity, 96,500 coulombs, is called 1 **Faraday.**

The interpretation of the facts summarized in Faraday's law is of the greatest importance. All of the solutions from which elements can be deposited by electrolysis must contain ions. Silver must be formed by discharge of the positive silver ion (Ag^+), hydrogen by the discharge of hydrogen ion (H^+), and copper by the discharge of the copper ion. But since twice as much electricity is required to discharge 1 gram molecule of copper ion as to discharge 1 gram molecule of hydrogen or of silver ion, there must be twice as much electricity on each copper ion as on a hydrogen or on a silver ion, for in equimolecular quantities there are equal numbers of atoms. This conclusion may be indicated by writing the formula of copper ion Cu^{++}. In the same way the conclusion is reached that the ions of iron in a ferrous solution must be Fe^{++}, while in a ferric solution they must be Fe^{+++}.

The valence of the elements in these compounds, then, seems to represent the number of unit charges of electricity contained on the ion of the element, and the reason why elements have different valences in different compounds is because the ions have different charges. When an iron atom goes over into ferrous ion, it loses 2 electrons; when it forms ferric ions, 3 electrons are lost. The difference in charge upon the ferrous and the ferric ions also explains the difference between the properties of ferrous and of ferric salts—since ferric ion contains

one less electron in its outer shell than does ferrous ion, the two substances must necessarily be different from one another, for the number of electrons determines the chemical properties.

Explanation of the Phenomenon of Electrolytic Conductivity and of the Accompanying Chemical Changes. Polarization.— The facts and theory presented in the preceding paragraphs make possible a very simple explanation of the passage of electricity through solutions and of the accompanying phenomena. As illustration, a solution of hydrogen chloride in water may again be chosen. Let the circuit consist of a battery connected by means of wires to platinum electrodes dipping into the solution. A current of electricity is believed to be a flow of electrons. A battery is a chemical device of such character that electrons are set free at its negative pole and used up at the positive pole. The electrons travel from the negative pole of the battery through the wire to the negative electrode in the solution. This solution contains positively charged hydrogen ions which are atoms of hydrogen that have lost 1 electron each. The hydrogen ions each take 1 electron from the electrode, and are thus reconverted into hydrogen atoms which at once combine to form hydrogen molecules. The hydrogen ions in the immediate neighborhood of the negative electrode are used up fairly quickly, but the charge on the latter attracts other hydrogen ions from other portions of the solution, and a stream of hydrogen ions toward the electrode is set up. If the hydrogen ions reach the electrode in sufficient numbers to take up the electrons, the current flows smoothly. But if electrons flow through the wire so fast that there are not enough hydrogen ions to take them up, electrons accumulate on the electrode, thus producing an obstacle to the flow of the current. This phenomenon is called **polarization.**[1]

Thus far nothing has been said about the chloride ions in the solution. They are repelled by the negative electrode, and diffuse away from it. When they come into contact with the other electrode, they give up their extra electron to it, and these liberated electrons flow through the wire to the positive pole of the battery,

[1] Polarization may be brought about in other ways also.

thus completing the circuit. The chloride ions, on giving up the electrons, become chlorine atoms and form chlorine molecules. The number of chloride ions around the positive electrode thus decreases, and other chloride ions diffuse toward the electrode to take their place. Polarization may occur at this electrode in the same way as at the other. The passage of electricity through any other solution may be explained in the same way.

Methods for Determining the Degree of Ionization.—It has been pointed out that dissociation of gaseous substances is frequently a reversible process which may reach equilibrium before dissociation is complete. It is of the greatest importance to determine whether this is true also of substances which dissociate into ions, and, if it is true, to find out how far ionization of various electrolytes proceeds. For this purpose any one of the methods by which the molecular weight of a substance in solution may be determined, or the conductivity of the solution may be employed.[1]

[1] There is, at present, considerable controversy and confusion about what is meant by " extent of ionization " of an electrolyte. According to present theories the formation of sodium chloride from the elements is accompanied by a transfer of an electron from the sodium atom to the chlorine atom. In this process sodium becomes sodium ion and chlorine chloride ion. The " molecules " of sodium chloride which are thought of as present in solid sodium chloride are (according to this view) merely aggregates of sodium and chloride ions held together by electrostatic charges. When a substance such as this dissolves in water, the ions already present become more or less separated from each other. If this picture is correct, " extent of ionization " is an indefinite expression, because it is not correct to assume that a certain fraction of the " molecules " are completely dissociated and the rest not dissociated at all. But there is another possible way in which ionization may be thought of. In the formation of the molecules from the elements, the electrons may be merely displaced from one atom toward the other. The complete severance of the electron from the one atom and its complete capture by the other may occur only when the substance is dissolved in a suitable solvent. In such a case only those molecules in which the transfer has been completed are ionized, and the idea " extent of ionization " becomes a definite one, for it refers to the fraction of molecules in which complete transfer has been accomplished. It is possible, though as yet by no means established, that strong electrolytes behave as postulated here for sodium chloride, and that weak electrolytes belong to the other type. See also pages 362, 363 and 366.

A substance completely dissociated into 2 ions has an apparent molecular weight of one-half of that expected if no dissociation occurs. If, however, the dissociation is not complete, the molecular weight actually observed lies between that corresponding to the formula of the substance and one-half that value. The **degree of ionization** of a substance is defined as the quotient of the number of molecules which have undergone ionization, by the number originally present in the substance. It is, in other words, the fraction of the solute ionized, and is usually designated by the Greek letter γ. It may be shown, if M represents the molecular weight corresponding to the formula of the substance, and M_0 the molecular weight experimentally observed in solution, that:

$$\gamma = \frac{M - M_0}{M_0}$$

for substances which yield 2 ions only. If the substance breaks up into more than 2 ions, the equation becomes:

$$\gamma = \frac{M - M_0}{(x - 1)M_0}$$

in which x is the number of ions formed by dissociation. What x is may be determined by noting whether M_0 approaches $\frac{1}{2}$ or $\frac{1}{3}$ or $\frac{1}{4}$ of M as the solution is diluted. (See pages 188 and 208.)

The conductivity of a solution of given concentration depends on the degree of ionization of the solute and upon the velocity with which the ions pass from electrode to electrode. Different ions move with very different speeds. When the difference of potential between the electrodes is 1 volt per centimeter, hydrogen ion travels through aqueous solutions at 18° at a rate of about 10.8 cm. per hour, hydroxide ion (OH^-) at about 5.6 cm. per hour, chloride ion at about 2.1 cm. per hour and sodium ion at about 1.26 cm. per hour. From the velocities of the ions, the conductivity of the completely ionized solution may be calculated. The degree of ionization is found by dividing the actual conductivity by the conductivity calculated for complete ionization. Details of the methods and calculations for determining the various quantities involved need not be described.

The Degree of Dissociation of Various Types of Electrolytes.—When the degree of dissociation of ionogens in a given

solvent, for example water, is determined by the methods just outlined, very great differences are found. Practically all salts, with the exception of a few of mercury and of cadmium, are almost completely dissociated into ions; the same is true of hydrochloric acid and of the other halogen acids (except hydrofluoric acid), of permanganic, and of nitric acid, as well as of bases such as sodium, potassium, barium, calcium, and magnesium hydroxides. It is to be noted that **solubility bears no relationship to degree of ionization**; thus, silver chloride or magnesium hydroxide are very insoluble, but the small amount that does dissolve is largely ionized. Not all bases or acids are highly ionized; all possible degrees of ionization are found. Hydrogen sulfide (H_2S) and hydrocyanic acid (HCN, also called prussic acid) are hardly ionized at all, acetic acid is much more highly ionized than these, and the degree of ionization of phosphoric acid lies between those of acetic and hydrochloric acids. Similar examples amongst the bases might be cited.

A list of the various ionogens containing the degree of ionization of each is very useful, since the relative extent of ionization of various ionogens frequently determines the course of reactions in which ions are involved, as is to be shown in the following chapter. But before such a list can be made, two points must be taken up in more detail.

The Degree of Ionization of Strong Electrolytes.—A number of phenomena associated with the behavior of the highly ionized or "strong" electrolytes have caused chemists to doubt that the methods of determining the degree of ionization described above should be applied to this class of ionogens. In such cases determinations of the degree of ionization by the molecular weight and the conductivity methods do not agree as well as they should. The strong electrolytes and their ions do not appear to obey the law of chemical equilibrium. (See page 172.) In the crystals of salts like sodium chloride the material points, which constitute the corners of the crystal structure, are not molecules of sodium chloride as one would expect if sodium chloride were un-ionized in the solid state, but seem to be the sodium and chloride ions. (See page 362.) Finally, in dilute aqueous solutions of strong electrolytes there are no known

properties which can be ascribed to the un-ionized molecules. Although these phenomena do not demonstrate beyond doubt that such electrolytes are completely dissociated, their degree of dissociation is surely so great that for the purposes of this text they may be looked upon as 100 per cent ionized. Since there is doubt as to the applicability of the methods of determining their degree of ionization, it may further be assumed that this is true for all concentrations of solutions. The correctness of this assumption is somewhat doubtful, at least in very many instances, but in qualitative discussions of the behavior of ionized solutions no important error will result from it.[1]

The Degree of Ionization of Weak Electrolytes.—No question has arisen about the correctness of the methods for determining the degree of ionization of the less highly ionized, or weaker electrolytes. In such cases, the degree of ionization depends not only on the nature of the electrolyte and that of the solvent, but also very largely on the concentration of the solution. As the solution becomes more and more dilute, the ionization becomes more and more nearly complete. Thus in a normal solution of acetic acid the latter is only about 0.4 per cent ionized, in a tenth normal solution 1.3 per cent, and in a hundredth normal solution 4 per cent ionized. This is just the relationship expected from Le Chatelier's rule. The process of dilution tends to decrease the number of molecules per unit volume of solution and, according to the rule, the system changes so as again to increase the number of molecules. This is possible only if a larger number of the undissociated molecules break up into ions.[2] All weak electrolytes in aqueous solution behave on dilution as does acetic acid. In such substances, the degree of ionization at various concentrations agrees with the quantitative statement of the law of chemical equilibrium given on page 172.

[1] See footnote, page 197. To this discussion may be added the suggestion recently made that the absence of properties which can be ascribed to the un-ionized substance may be due to the effect of water in masking these properties.

[2] Ions are charged molecules. They affect the properties of solutions, such as lowering of vapor tension, etc., just as do any other molecules.

The Degree of Ionization of Electrolytes which Yield more than two Ions.—Such substances as sulfuric acid or phosphoric acid ionize in several stages. This is represented by the equations:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^-, \qquad HSO_4^- \rightleftarrows H^+ + SO_4^{=}$$

and

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-, \quad H_2PO_4^- \rightleftarrows H^+ + HPO_4^{=}$$

$$HPO_4^{=} \rightleftarrows H^+ + PO_4^{\equiv}$$

In all cases the first reaction proceeds most readily. Consequently, in a concentrated solution of phosphoric acid there are chiefly hydrogen ions and di-acid phosphate ions, $H_2PO_4^-$; as the solution becomes more dilute the latter also dissociate appreciably; and in very dilute solutions the phosphate ion, $PO_4^{\equiv}$ is present in considerable amount.

Classification of Some Ionogens according to their Degree of Ionization.—In the following table various electrolytes are grouped according to their degrees of ionization. The first list gives the strong electrolytes which, for the reasons mentioned, are to be treated in this text as 100 per cent ionized. In the other lists the degree of ionization, in terms of per cent of the solute ionized in 1/10 normal aqueous solution, is given after the solute. For substances like sulfuric and phosphoric acids which ionize in steps, the stage of ionization to which the fraction ionized refers is indicated by placing the products of ionization in parentheses after the name of the substance.

TABLE X

DEGREE OF IONIZATION OF ELECTROLYTES

A. Substances which may be looked upon as 100 per cent ionized.

ACIDS: Hydrochloric, hydrobromic, hydriodic, nitric, permanganic, chloric, perchloric, sulfuric.*

BASES: The hydroxides of sodium, potassium, lithium, magnesium, calcium, strontium, barium.

SALTS: Practically all salts, with the exception of some mercury and possibly some cadmium and lead salts.

* Sulfuric acid is much weaker than the other acids of this group.

B. Moderately strong electrolytes. Per cent ionization refers to N/10 solution.

Acids: Phosphoric (H^+, $H_2PO_4^-$) 27 per cent; oxalic (H^+, $HC_2O_4^-$) 50 per cent; hydrofluoric, 8.5 per cent; acetic, 1.3 per cent.

Bases: Ammonium hydroxide, 1.3 per cent. The following bases are moderately strong electrolytes, but, as they are not soluble in water, their degree of ionization is, in most cases, not accurately known: the hydroxides of silver, copper, cadmium, zinc, nickel, cobalt, manganese and ferrous iron.

Salts: Mercuric chloride.

C. Weak electrolytes.

Acids: Carbonic (H^+, HCO_3^-) 0.17 per cent; hydrogen sulfide (H^+, HS^-) 0.07 per cent; hydrocyanic, 0.01 per cent; boric (H^+, $H_2BO_3^-$) 0.01 per cent; hypochlorous, 0.02 per cent.

Bases: Most of the common inorganic bases are very slightly soluble in water and their degree of ionization is in most cases not exactly known. The following are weak bases: the hydroxides of mercury, bismuth, aluminium, chromium, and ferric iron.

Salts: Mercuric cyanide is only very slightly ionized.

Evidently, the preceding table is incomplete. Further information will be given when the various acids and bases are studied individually. The division into strong, moderately strong and weak electrolytes is arbitrary, as the various groups merge into each other. The discussion of sulfuric and of phosphoric acids makes it clear that in all the acids which ionize in steps, the second ionization is less than the first. The analogous relation holds also for bases. Sulfuric acid in concentrated solutions yields chiefly hydrogen and acid sulfate (HSO_4^-) ions; a base like bismuth hydroxide chiefly $Bi(OH)_2^+$ and OH^- ions.

The Ionization of Water.—Although the conductivity of water is very slight, even the purest obtainable does conduct electricity. Hence, it must be concluded that water is ionized, even though only to a minute extent. By various methods it has been shown that the ionization of pure water is approximately 2×10^{-7} per cent. The importance of this fact will be discussed in Chapter XV.

Ionization in Solvents Other than Water. The Rôle of the Solvent in Ionization.—Since positively and negatively charged bodies attract and discharge one another, it might be asked why

this discharge does not occur in the case of the positively and negatively charged ions which exist side by side in solution.[1] In all probability the solvent prevents this. All solvents in which ionization occurs are liquids of high dielectric constant. Surrounding the charged body by a layer of a dielectric material of this sort would decrease the tendency to discharge. Possibly also the solvent forms a rather unstable compound with the ions, and this compound formation may prevent the electrons from passing back from the negative ion to the positive ion—that is, may prevent discharge of the ions. Common ionizing solvents other than water are sulfuric acid (very concentrated), formic acid, liquid ammonia, and alcohols, mentioned in the order of decreasing ionizing strength. Fused salts are excellent ionizing media, and all salts in the fused state seem to be practically 100 per cent ionized. The function of the solvent in ionization is, however, not fully understood. Thus in formic acid (which has a fairly high dielectric constant), solutions of salts are highly ionized, but hydrogen chloride acts as a moderately weak electrolyte although in water it is very highly ionized. Further specific effects of the solvent will be encountered in later chapters.

EXERCISES

(1) (*a*) What reason is there for believing that salts, acids and bases are dissociated in aqueous solutions? (*b*) Why are these reasons by themselves not sufficient to demonstrate the dissociation of such substances in aqueous solution?

(2) (*a*) What reasons are there for believing that positively and negatively charged particles exist in aqueous solutions of salts, acids and bases? (*b*) Why are the facts stated not sufficient to prove that the positively and negatively charged particles are the result of dissociation?

(3) What is the evidence that salts, acids, and bases, are dissociated into positively and negatively charged particles?

(4) In what respect does the passage of an electrical current through a metal differ from the passage through a solution?

(5) Explain the passage of a current of electricity through a solution by the theory of ionization.

[1] The discharge of ions differs from the discharge of substances which have been charged by physical means, because discharge of ions is a chemical reaction.

(6) Explain the origin of the charges on ions in terms of the electron theory of matter. Confine your explanation to the case of the ions of salts like sodium chloride.

(7) (*a*) Why must we assume that the numbers of positive and negative ions in a solution are always such that the number of positive charges is equal to the number of negative charges? (*b*) Is this statement the same as saying that the number of positive ions is equal to the number of negative ions? Why?

(8) (*a*) What is the relationship between the valence of the metallic constituent of a salt and the number of charges on the ion? (*b*) What experimental evidence leads to the conclusions that some ions carry one unit of charge and others 2, 3 and so on, unit charges?

(9) How much copper is deposited from copper sulfate solution if the solution is electrolyzed with a current of 10 ampères for one hour between platinum electrodes? (*Ans.* 11.86 grams.)

(10) (*a*) How much silver is deposited from silver nitrate solution by passing through it a current of 0.5 ampère for three hours between platinum electrodes? (*b*) How much silver is dissolved from a silver anode if a current of 2 ampères is passed for one hour through the solution into which the anode dips?

(11) Calculate the amounts in grams of the following substances deposited by the indicated flow of current:

(*a*) Iodine from potassium iodide by 0.6 ampère for 50 minutes.

(*b*) Antimony from antimony trichloride ($SbCl_3$) by 5 ampères for two hours.

(*c*) Hydrogen from hydrochloric acid by 15 ampères for two hours.

(12) Give the formulae and names of the ions of the following salts. (In writing the formulae, indicate by + and − signs above the symbol whether the ions are positive or negative, and by the number of + and − signs, the number of unit charges carried by each ion): sodium bromide, potassium fluoride, calcium nitrate, potassium permanganate, potassium dichromate, sodium sulfide, barium sulfate, zinc chloride, mercuric bromide, mercurous iodide.

(13) (*a*) Give in general terms two methods for determining the degree of ionization of electrolytes. (Description of the methods is not necessary.) (*b*) How may the number of ions into which a substance dissociates be determined?

(14) What is the meaning of the term "strong electrolytes"? Give two reasons justifying the assumption that, for qualitative purposes, strong electrolytes may be considered to be 100 per cent ionized.

(15) (*a*) Write equations representing the steps by which the substance H_2CO_3 ionizes. (*b*) Which ionization is more nearly complete?

(16) Why are the terms "strong" or "weak" salts never used?

(17) How would you classify each of the following substances in regard to the extent of ionization: sulfuric acid, sodium chloride, carbonic acid, barium sulfate, ammonium hydroxide, silver chloride, hydrogen sulfide, hydrochloric acid, sodium hydroxide, barium nitrate, barium hydroxide, aluminium hydroxide, prussic acid, potassium cyanide?

REFERENCES

MILLARD—Physical Chemistry for Colleges, pages 145–166, gives details concerning the theory of ionization and methods of determining degree of ionization.

CARTLEDGE—Inorganic Physical Chemistry, pages 155–172, covers the same ground somewhat more descriptively.

MOORE—History of Chemistry, pages 234–251, writes interestingly of the development of the theory of ionization.

MELLOR—Comprehensive Treatise, Vol. I, pages 962–993, gives a wealth of material, interesting both from the historical and practical point of view, about the theory of ionization and the proofs on which it rests.

CHAPTER XIV

THEORY OF IONIZATION, II

Methods of Determining the Composition of Ions.—The Properties of Ions.—Electromotive Series.—Oxidation and Reduction

Thus far in the presentation of the theory of ionization, very little has been said about its chemical aspects. The assumption that ions possess independent physical and chemical properties has been shown to be compatible with modern views concerning the structure of atoms, but no proof of the assumption has been given. The theory has been of the greatest value to the chemist in explaining and coordinating a large number of chemical phenomena. It explains so many of the phenomena met by the beginner in chemistry that he is likely to draw the erroneous conclusion that all reactions are due to ionization. This misunderstanding arises because ionic reactions are chosen, on account of their simplicity, as the material for most introductory courses in chemistry. Probably just as many reactions are not of the ionic type—most of the chemical changes in living organisms, most of the chemical processes in the manufacture of dyes, explosives and plastics, to choose but a few illustrations, are not ionic reactions in the ordinary sense of the word. It is of course likely (as will be pointed out in the chapter on the structure of atoms and molecules) that ionic and non-ionic reactions represent extremes, and that intermediate types exist.

Characteristics of Ionic Reactions.—Salts, acids and bases, that is, substances which are shown by their low molecular weights and their conductivity in solution to be ionized, are invariably capable of reacting by **double decomposition.**[1] Double decompositions between ionized substances proceed at

[1] This term is defined on page 165.

an immeasurably great velocity. Thus, when an aqueous solution of sodium chloride is added to a similar solution of silver nitrate, silver chloride and sodium nitrate are formed so rapidly that, so far as anyone has been able to determine, the reaction is instantaneous. Chloroform, which has a normal molecular weight and is a non-conductor, also reacts with silver nitrate. Although the percentage of chlorine in chloroform ($HCCl_3$) is very much greater than that in sodium chloride, the formation of silver chloride from the former proceeds only at elevated temperatures, best in the presence of nitric acid, and so slowly that days are required to complete the reaction. In this case the reaction is not one of double decomposition; but even those non-ionic reactions formulated as double decompositions are likely to be slow. Unquestionably there are some rapid non-ionic reactions—for example, the one between hydrogen and oxygen at high temperatures, and other explosive reactions; but it is a question whether even these very rapid non-ionic reactions have as high velocities as double decompositions between ionogens.

Methods of Determining the Composition of Ions.—The composition of the ions can usually be determined without difficulty when the dissociating molecules consist of only 2 atoms. For example, the simplest assumption in the case of hydrogen iodide is dissociation into hydrogen and iodide ions. This assumption is verified, and the kind of charge on each of the 2 ions discovered, by observing the products formed at platinum electrodes when an aqueous solution of the substance is electrolyzed. At the negative pole hydrogen is formed by discharge of positive hydrogen ions, and at the positive pole, iodine is deposited by discharge of negative iodide ions. Electrolysis of aqueous solutions of sodium chloride between platinum electrodes does not lead to such clear-cut results. Chlorine is liberated at the positive pole, showing that one of the products of dissociation is negative chloride ion. The other ion is unquestionably positive sodium ion, but even if it were discharged as metallic sodium at the cathode, the liberated sodium could not be isolated because it would immediately react with the water to give hydrogen and sodium hydroxide. The difficulty may be avoided in several ways.

If, for example, mercury is used as the negative pole, the liberated sodium dissolves in the mercury, and the resulting solution acts on water so slowly that the presence of sodium can be demonstrated without difficulty. The presence of water might be avoided by electrolyzing molten sodium chloride, but other difficulties would then be encountered because of the high temperature.

When substances, the molecules of which consist of more than two kinds of atoms ionize, it is necessary to study the behavior of the substance thoroughly before deciding what the ions are. Without experimental facts to guide one, it might be believed that sodium nitrate ($NaNO_3$) could break up into sodium, nitrogen and 3 oxygen ions. But the apparent molecular weight of the substance in very dilute aqueous solution is never less than one-half the calculated value. This indicates that the molecule breaks up into 2 ions only. On electrolysis, with mercury as the negative electrode, a solution of sodium in mercury is formed, thus showing that sodium ion is one of the two components of the solution. Hence, only one possible combination, NO_3^-, is left for the negative ion. This conclusion may be verified by studying the chemical behavior of the substance in solution. In all double decompositions in which sodium nitrate takes part, the nitrogen and the 3 oxygen atoms remain together—the group NO_3 acts almost as a unit.[1] Further verification of the composition of the negative ion is the fact that the concentration of nitrate around the positive pole increases during electrolysis as a result of the migration of nitrate ions toward this pole.

Products of Electrolysis.—Products of electrolysis which remain unchanged at the electrodes or escape unchanged from the solution, are often called **primary** products. In this group are included elements like hydrogen, the atoms of which combine with each other to form molecules. In many cases, however, the products of electrolysis react with the solvent or with the electrodes, and thus give rise to **secondary** products. If, for example, an aqueous solution of sodium chloride is electrolyzed with a copper anode, the liberated chlorine acts with the cop-

[1] In certain other types of reactions the nitrate group may be broken up. This is discussed in the chapters on oxidation and reduction and on nitric acid.

per, forming cupric chloride. If platinum electrodes are used, the chlorine acts to a limited extent with water, forming hypochlorites, and these may, at elevated temperatures, decompose into chlorates as described on page 377. The formation of sodium hydroxide and hydrogen at the negative pole during electrolysis of an aqueous solution of sodium chloride was formerly (and by some chemists still is) interpreted in a similar way. That is, it was assumed that sodium is liberated, and then reacts with water. Sodium has, however, a much greater tendency to remain in the ionic condition than has hydrogen. (See also pages 215 and 561.) The aqueous solution surrounding the negative pole always contains some hydrogen ions. Since they are more readily discharged by the current than are sodium ions, hydrogen is formed on electrolysis and sodium ions are left in solution. When hydrogen ions are discharged, the hydroxide ions of the water are left free, and they pair with the sodium ions brought by the current to the electrode.

In the same way the formation of nitric acid at a platinum anode during electrolysis of sodium nitrate may be explained. Nitrate ions are apparently difficult to discharge. Consequently, the current discharges the hydroxide ions present in the water surrounding the anode in any aqueous solution. The hydrogen ions thus left free pair with the nitrate ions brought to the electrode. The discharged hydroxide ions cannot, however, exist as neutral molecules, but break up into water and oxygen according to the equation:

$$4OH \rightarrow 2H_2O + O_2$$

The ions of all the more active metals, especially those of the alkali and alkaline earth groups, behave like sodium; all of the compound ions like sulfate, $SO_4^{=}$, phosphate, $PO_4^{\equiv}$, chlorate, ClO_3^{-} and so on, behave like nitrate ion. In other words, they are not discharged in aqueous solution, but allow the hydrogen ion or the hydroxide ion, respectively, to discharge in their place.

The nature of the electrode is also of great importance in determining the products of electrolysis. If copper electrodes are used during electrolysis of sodium nitrate, nitric acid is not formed at the anode. In this case it is easier for the current to

force copper atoms to go over to copper ions at the electrode than it is to discharge hydroxide ions. The copper ions pair with the nitrate ions brought to the electrode by the current, and copper nitrate is formed. At a silver anode, silver nitrate would be formed in similar fashion. But platinum does not readily go over to the ionic condition; the current therefore discharges hydroxide ions at a platinum anode, and no platinum nitrate is obtained. Similar phenomena occur when sodium sulfate, or sulfuric acid, or phosphates, etc., are electrolyzed between the various types of electrodes described.[1]

Methods of Discovering the Chemical Properties of Ions. Hydrogen Ion.—The methods and logical processes employed in determining the properties of the ions are presented most clearly by means of an example. For this purpose, hydrogen ion may be chosen. It is well known that all substances which behave as acids contain hydrogen. The reverse of this statement is not true. For example the hydrocarbons like methane or propane (C_3H_8), which contain a large number of hydrogen atoms per molecule, have none of the properties of acids. Hence, the mere presence of hydrogen in a substance does not make it an acid. On the other hand, molecular weight and conductivity methods show that all acids are ionized to a greater or less extent. On electrolysis, solutions of all acids yield hydrogen at the negative pole. These facts demonstrate that all acids contain hydrogen ion. Since all acids have one substance, hydrogen ion, in common, and since they all possess properties in common, these common properties must be the properties of the hydrogen ion.

The argument is especially well illustrated in the case of hydrogen chloride. This substance is a gas at ordinary temperatures; it exists also in solution in solvents like toluene or benzene, and it may be dissolved in water. In the gaseous state, and in toluene or benzene solutions, if it is absolutely free from moisture,

[1] Concentration of the solution and voltage applied at the electrodes may also influence the products of the electrolysis. If in the electrolysis of a dilute solution of hydrochloric acid a low voltage is employed, oxygen is liberated at the anode. This is due to the fact that hydroxide ions are discharged at a lower voltage than are chloride ions, and yield oxygen as described in the text.

it displays the normal molecular weight and is a non-conductor; ions cannot be present in gaseous hydrogen chloride or in these solutions. Gaseous hydrogen chloride or its solution in these non-ionizing solvents does not display acid properties as the term is ordinarily used—e.g., it does not react with iron, with perfectly dry bases, or with calcium carbonate. The solution of hydrogen chloride in water is a conductor of electricity, and the molecular weight of the solute indicates extensive dissociation. This solution is a strong acid; iron and all the other more active metals are attacked by it, forming the chloride of the metal and liberating hydrogen; bases are neutralized; calcium carbonate reacts with the formation of carbon dioxide and calcium chloride.[1]

Strength of Acids and Degree of Ionization.—The conclusion reached in the preceding discussion is that in aqueous and similar solutions acids owe their characteristic properties to the hydrogen ion. This conclusion is corroborated by the relationship between the strength of the acid and its degree of ionization. Strong and weak acids may be differentiated as follows. The former react *rapidly* with metals like iron, while the latter act slowly; strong acids affect indicators decidedly while weak acids have only a slight effect; strong acids displace weaker acids from the salts of the latter, and completely neutralize bases. The last two points are discussed in detail in the chapter on equilibrium in ionic reactions. (See pages 226–228 and pages 229–233.) For the present it is sufficient to note that there are definite reasons for calling certain acids stronger than others. Thus hydrochloric acid is a very strong acid, phosphoric acid is weaker, acetic acid still weaker, and prussic acid the weakest of the four. Reference to the table of degrees of ionization in the preceding chapter shows that the order of strength of the acids

[1] In demonstrating the difference in behavior of dry hydrogen chloride and its aqueous solutions, moisture must be most carefully excluded from the former. This is difficult with the gaseous substance but may be readily accomplished in the case of the toluene solution. The solution is prepared by passing hydrogen chloride (generated in the usual way and passed through concentrated sulfuric acid for additional drying) into toluene dried with fused calcium chloride. The calcium chloride is left in the solution until it is to be used. Of course, the usual precautions for excluding moisture during the preparation and storage of the solution must be observed.

is also the order of the degree of ionization. In other words, the more completely a substance breaks up into hydrogen ions the more strongly does it display acid properties—an unanswerable proof that the ordinary acid properties are the properties of the hydrogen ion.

Nature of Bases. Strength of Bases.—All the substances called bases contain both hydrogen and oxygen; in all double decomposition reactions in which bases take part, the oxygen and the hydrogen atoms in the ratio of 1 to 1 (OH), act as a unit. Sodium hydroxide is shown by molecular weight determination in aqueous solution to be ionized into 2 ions, and to yield as one of these the positive sodium ion. Hence, the other ion must be negative hydroxide ion (OH^-).[1] The formation of oxygen at the anode on electrolysis is easily explained on this assumption. The " free radical " OH, formed there by discharge of OH^-, decomposes according to the equation,

$$4OH \rightarrow 2H_2O + O_2$$

Much evidence of this type has convinced chemists that the substance responsible for the characteristic behavior of all bases —a behavior which the student should attempt to recall for himself—is due to the hydroxide ion only. Strong bases are highly ionized, and weak bases are ionized to only a small extent.

Quantitative Relationships between Degree of Ionization and Strength of Bases and of Acids.—In this text only the qualitative relationship between the strength of acids and of bases can be presented. But the strength of such substances can be accurately measured. If this is done, and the ratio of these strengths is calculated, it is found that this ratio is the same as that obtained from the respective degrees of ionization of the two acids or bases. This concordance of results depending on such widely different types of experiments as molecular weight determinations, conductivity measurements, and studies of relative chemical activity is one of the strongest pieces of evidence in favor of the theory of ionization.

[1] Sodium hydroxide is sometimes called sodium hydrate, and similar names are used for other bases. This terminology is absolutely indefensible.

Some Definitions in Terms of the Theory of Ionization.—The theory of ionization leads to a very simple definition of what acids and bases are. In a similar way the following terms may be interpreted. **A polybasic acid** is a substance which yields more than 1 hydrogen ion per molecule, a **polyacid** base yields more than 1 hydroxide ion per molecule.[1] A **normal salt** ionizes into positive and negative ions other than hydrogen or hydroxide ions. An **acid salt** yields two or more different kinds of positive ions of which at least one is hydrogen ion; it may be looked upon as formed by the incomplete neutralization of a polybasic acid. A **basic salt** yields two or more different kinds of negative ions of which at least one is hydroxide ion; it may be looked upon as formed by the incomplete neutralization of a polyacid base. A **mixed salt** contains more than one kind of positive ion or more than one kind of negative ion, none of which is hydrogen ion or hydroxide ion. The student should find examples of each type of ionogen here defined. According to these definitions, **water** is both a very weak acid and a very weak base. The importance of this fact will be brought out in the chapter on Equilibrium in Ionic Reactions.

Ionic Displacements.—In studying the methods of preparation of hydrogen, the reaction whereby the element is displaced from water or acids by metals was encountered. An illustration is the action of zinc on hydrochloric acid. Two of the substances involved in the reaction, namely, hydrochloric acid and zinc chloride, belong to the group of highly ionized electrolytes which, for practical purposes, may be looked upon as being 100 per cent ionized in dilute aqueous solution. When this fact is taken into consideration, the reaction equation becomes:

$$Zn + 2H^+ + 2Cl^- \rightarrow Zn^{++} + H_2 + 2Cl^-$$

The chloride ions have evidently undergone no change, and the reaction consists merely in the transfer of the two positive charges

[1] The term "polybasic acid" was originally devised to indicate that 1 gram molecule of such an acid, e.g., sulfuric acid, could neutralize more than 1 gram molecule of a base like sodium hydroxide. The term "polyacid base" had a similar origin.

from the hydrogen ion to the zinc atom. This statement is equivalent to saying that the zinc atom has given up 2 electrons to the hydrogen ions. When hydrogen ions take on electrons they become neutral hydrogen atoms which, in turn, unite with each other to form hydrogen molecules. Apparently, then, zinc atoms have a greater tendency to give up electrons than have hydrogen atoms.

By applying the same sort of reasoning to the behavior of copper towards acids, the opposite conclusion is reached. Since copper does not replace hydrogen, it is incapable of giving electrons to hydrogen ions, and must have a smaller tendency to lose electrons than hydrogen has. If this is true, copper atoms must lose electrons much less easily than do zinc atoms. Zinc ought, therefore, when placed in contact with copper ions, to give up electrons to the latter, and convert them into metallic copper. The reaction:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

is known to every beginner in chemistry. Written in terms of the theory of ionization it becomes:

$$Zn + Cu^{++} + SO_4^{--} \rightarrow Zn^{++} + Cu + SO_4^{--}$$

The predicted reaction occurs; zinc takes the positive charge from copper ion by transferring 2 electrons to the latter. By similar reasoning the conclusion is reached that sodium atoms lose electrons more readily than zinc atoms. Sodium displaces hydrogen from water, which contains only traces of hydrogen ion, while zinc does so only from acids which yield a high concentration of hydrogen ion. Sodium should therefore be able to displace both zinc and copper from their salts. These reactions actually occur if precautions are taken to prevent the violent action of sodium on the water used as solvent for the salts.[1]

Electromotive Series of the Metals and their Chemical Activity.—A study of displacement reactions from the point of view described reveals the relative ease with which the atoms

[1] The reaction may be demonstrated by using sodium amalgam in place of pure sodium.

of metals lose electrons. From these data a table may be prepared in which the metals are arranged in this order, those losing electrons most easily being at the head of the list. This list is given in the following table of the "Electromotive Series of the Metals." The exact reason for the name will be explained in a later chapter. The order in which the metals appear in this table is the same as that in which they were placed in the tables

TABLE XI

ELECTROMOTIVE SERIES

(Approximate order according to displacement. For exact Table, see page 557.)

K	Mn	Sn	Hg
Na	Zn	H	Ag
Ba	Fe	Cu	Pt
Ca	Cd	Sb	Au
Mg	Ni	Bi	
Al	Pb		

based on their relative activity toward oxygen, toward acids and water, and on the stability of their oxides and hydroxides. Evidently the fundamental property responsible for the recurrence of this order in so many reactions is the ease with which the elements lose electrons. How this property is related to the displacement of hydrogen has already been discussed. The connection is just as simple in the reaction of the metals with oxygen. The oxides are unquestionably compounds in which the metal is the positive and the oxygen the negative constituent. When metal and oxygen unite, the metal gives up electrons (thus becoming positively charged), and the oxygen takes up the electrons (thus becoming negatively charged). The more readily a metal loses electrons, the more readily it must react with oxygen. On the other hand, the decomposition of an oxide involves the regaining of the lost electrons by the metallic constituent of the oxide. Those metals which have no particular tendency to lose electrons must, therefore, readily revert from the state of positive ion to that of neutral metal. For this reason

mercuric oxide easily gives up oxygen. In the oxide, the mercury is positive and the oxygen negative, because 2 electrons have been transferred from each mercury atom to each oxygen atom. Mercury has no great tendency to lose these 2 electrons. They can therefore become detached from the oxygen and return to the mercury, leaving the former as free oxygen and the latter as free mercury.

This tendency to lose electrons is responsible for many other activities of the metals. When they react with halogens, salts are formed, and in these the metallic constituent is the positive ion and the halogen the negative ion. Evidently this reaction is a transfer of electrons from the metal to the halogen, and consequently those metals which react most easily with oxgyen, which displace hydrogen most readily, which have the most stable oxides, ought also to react most readily with the halogens, and to form the most stable halides. That this is actually the case was shown in Chapter XI.

Electromotive Series for Non-metals.—Thus far reactions involving transfers of electrons have been discussed only from the point of view of the ease with which one of the atoms involved gives up electrons. Obviously the readiness of the other atoms to take up these electrons is just as important a factor in the reaction. Fluorine displaces chlorine, bromine and iodine from their salts, chlorine displaces bromine and iodine, and bromine displaces iodine. The reaction for the displacement of bromine by chlorine in terms of the ionization theory is:

$$Cl_2 + 2Na^+ + 2Br^- \rightarrow 2Cl^- + 2Na^+ + Br_2$$

The sodium ion undergoes no change, and the whole reaction is summarized in the statement that chlorine acquires a negative charge by taking it from the bromide ion. This may be interpreted to mean that chlorine atoms have a greater tendency to take on electrons than have bromine atoms. The other displacements mentioned above, lead to the conclusion that fluorine atom has the greatest tendency to take on electrons, and iodine the least. Hence, fluorine ought to be most active in its reactions with metals, and iodine the least—an order which agrees with the facts.

Oxidation and Reduction from the Ionic and Electronic Point of View.—The simplest case of an oxidation is that of the interaction of oxygen with a metal. The oxygen, as the name oxidation implies, is the oxidizing agent; the metal must be the reducing agent, since, by definition, a reducing agent is a substance which is capable of being oxidized. It has been pointed out that the fundamental change in this reaction is the transfer of electrons from the metal, that is from the reducing agent to the oxidizing agent. Generalization of this idea leads to the statement that **an oxidizing agent is a substance which contains an atom or an ion capable of taking up electrons, and that a reducing agent is a substance which contains an atom or an ion capable of giving up electrons.** For this reason the active metals, which give up electrons most readily, are the most powerful reducing agents, while elements like fluorine and chlorine, the atoms of which have a pronounced tendency to become negative ions by taking up electrons, are powerful oxidizing agents.

This interpretation of the phenomena of oxidation and reduction has proved so useful in chemistry that its further elaboration is left to a later chapter, when more experimental material will be at hand. But in order that the student may clearly understand the electronic theory of oxidation and reduction, a few more illustrations will be cited here.

When iron is treated with dilute hydrochloric acid, in the absence of oxygen, ferrous chloride ($FeCl_2$) and hydrogen are formed. By the methods employed in the preceding discussion the student may convince himself that the essential change is represented by the equation:

$$Fe + 2H^+ \rightarrow Fe^{++} + H_2$$

The iron atom has given up 2 electrons to 2 hydrogen ions. Iron, the reducing agent, is oxidized in this reaction. If the solution is now treated with chlorine, ferrous chloride is converted into ferric chloride, and this reaction is again one of oxidation and reduction.[1] The equation for this last reaction, in terms

[1] That both of these reactions involve oxidations in terms of the older definition of the word may be seen from the following. When iron is exposed to a limited amount of oxygen, ferrous oxide is formed by oxidation of the

of the ionization theory, is:

$$2Fe^{++} + 4Cl^- + Cl_2 \rightarrow 2Fe^{+++} + 6Cl^-$$

Of the 6 chloride ions on the right side of the equation, only 2 are new, since the other 4 were present in the original ferrous chloride. These 2 new chloride ions are formed at the expense of the chlorine atoms which take on 1 electron each. The source of the electrons is easily discovered. Iron was originally present in the ferrous state, i.e., as Fe^{++}. By the reaction, 2 ferrous ions are converted into 2 ferric ions, Fe^{+++}. According to the theory of atomic structure employed in this discussion, the only way in which this change could have been brought about is by loss of an additional electron from each ferrous ion. The change which converts iron into ferrous chloride may be put into the equation:

$$Fe \rightarrow Fe^{++} + 2\epsilon$$

and the change of ferrous chloride into ferric chloride into the equation:

$$Fe^{++} \rightarrow Fe^{+++} + \epsilon.$$

That electrical changes are actually involved in reactions of oxidation and reduction may be demonstrated experimentally. Two platinum electrodes connected respectively with the positive and the negative pole of a battery, are dipped into a solution of ferrous chloride. When the current has flowed for a few minutes, the solution in contact with the positive electrode is partially converted into ferric chloride, and iron is found on the negative electrode. The current is acting as the oxidizing and

iron ($2Fe + O_2 \rightarrow 2FeO$). Ferrous oxide (FeO) may be converted into ferrous chloride by the action of hydrochloric acid ($FeO + 2HCl \rightarrow FeCl_2 + H_2O$). The latter reaction is simply the neutralization of a basic oxide by an acid; it involves no process of oxidation or reduction. Hence ferrous chloride represents the same stage of oxidation as does ferrous oxide. Now ferrous oxide, when heated with an excess of oxygen may be converted into ferric oxide, Fe_2O_3—manifestly a reaction of oxidation. The ferric oxide may be neutralized by hydrochloric acid to form ferric chloride ($Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$). Hence the change from ferrous chloride to ferric chloride involves oxidation of the former.

reducing agent. At the negative pole, where it furnishes electrons to the solution, the ferrous ions are reduced to iron; at the positive pole where the current removes electrons from the solution, ferrous ions are oxidized to ferric. The experiment fits in with the definition,—at the point at which the current **takes electrons** out of the solution, it is an **oxidizing agent;** at the point at which it **gives electrons** to the solution it is a **reducing agent.**

A similar illustration of the relationship between oxidation and reduction on the one hand and electrical phenomena on the other was encountered in the method of preparation of the halogens. Chlorine may be prepared either by oxidation with chemical reagents or by electrolysis of chlorides. But the latter method is really also an oxidation. When sodium chloride in aqueous solution is electrolyzed, chlorine is formed at the positive electrode. This is the electrode at which the current removes electrons, and by taking them from the chloride ions, it **oxidizes** the latter to free chlorine. Fluorine has the greatest tendency of all elements to take on electrons. On this account no substance is capable of taking the electrons away from the fluoride ion, and fluorine can therefore not be prepared by chemical oxidation of fluorides. But the electrical current can remove electrons even from fluoride ions, and consequently produce elementary fluorine.[1]

One more illustration may be chosen. Although certain oxides, such as manganese and lead dioxides, liberate chlorine from chlorides, this is by no means a general property of oxides. Lead monoxide or manganous oxide do not react in this way. Examination of the equation for any reaction in which an oxide liberates chlorine from a chloride shows two important changes. The chloride ion loses negative charges becoming neutral chlorine, and the metallic constituent of the oxide changes valence. In the case of manganese dioxide, the equation is

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

In manganese dioxide, manganese has a valence of 4 positive (since each oxygen is 2 negative), while in manganous chloride

[1] A very excellent set of experiments to demonstrate the connection between oxidation and reduction and current production is described in Stieglitz, Qualitative Analysis, Vol. I.

its valence is only 2 positive. Losing 2 positive charges is equivalent to taking up 2 electrons. Again the oxidizing agent, in this case the tetravelent manganese ion (Mn^{++++}), takes up electrons and the reducing agent (Cl^-) gives up electrons. Further study of reactions of this type reveals the fact that **all reactions of oxidation and reduction may be explained by assuming that they are accompanied by changes in valence** which agree with the electronic definitions of oxidation and reduction.

EXERCISES

(1) In general how do reactions between ionogens differ from reactions between un-ionized substances?

(2) Describe how you would determine the composition of the positive and of the negative ions of the following salts: potassium bromide, potassium sulfate, copper nitrate, potassium permanganate, sodium hydroxide.

(3) What are the products formed at (*a*) the anode, and (*b*) the cathode when each of the following substances is electrolyzed in aqueous solution between platinum electrodes? It will be found convenient to answer in tabular form, thus:

(substance electrolyzed) (products at anode) (products at cathode)

Sodium chloride, silver nitrate, copper sulfate, potassium fluoride, barium hydroxide, sodium acid phosphate (Na_2HPO_4), calcium iodide, potassium chlorate. Give an explanation of the formation of each product.

(4) (*a*) What are the products of electrolysis if an aqueous solution of silver nitrate is electrolyzed between silver electrodes? (*b*) What are the products if copper sulfate is electrolyzed between copper electrodes? Explain.

(5) Give all of the evidence that acid properties are the properties of hydrogen ions.

(6) What are the properties of hydroxide ions?

(7) (*a*) Which positive ions have a marked tendency to unite with hydroxide ion? (*b*) Do these ions have a marked tendency to unite with negative ions other than hydroxide? (*c*) If so, which ones?

(8) What negative ions have a marked tendency to unite with hydrogen ions?

(9) Define the following expressions, in terms of (*a*) the behavior of the substance, and (*b*) the theory of ionization: salt, acid salt, polybasic acid, normal salt, basic salt.

(10) What is the evidence that atoms of zinc lose electrons more readily than do atoms of copper, and less readily than do atoms of sodium?

(11) What is the essential change in each of the following reactions: (*a*) $Cl_2 + 2KI \rightarrow 2KCl + I_2$; (*b*) $Cu + Hg(NO_3)_2 \rightarrow Hg + Cu(NO_3)_2$. In answering formulate each reaction as an ionic one, and explain why you answer as you do.

(12) Define from the electronic point of view the following terms: (*a*) oxidation of a substance, (*b*) oxidizing agent, (*c*) reduction of a substance, (*d*) reducing agent.

(13) Why must one substance always be reduced when another is oxidized?

(14) In the two equations in question (11), which substances are oxidized and which reduced?

(15) Show that in reactions in which you know that oxidations and reductions occur, these changes are correctly interpreted by the electronic concept of oxidation and reduction. (Choose only simple cases, for example, oxidations in which oxygen, chlorine or bromine are the oxidizing agents. Substances like permanganates and nitric acid are to be discussed later.)

REFERENCES

The references to Chapters XIII and XV should be consulted. In addition

HILDEBRAND—Principles of Chemistry, Chapter X.

MELLOR—Modern Inorganic Chemistry, Vol. I, Chapter XVI, will be found helpful.

CHAPTER XV

EQUILIBRIUM RELATIONS IN IONIC REACTIONS

Neutralization.—Hydrolysis.—Indicators.
Non-aqueous Solvents

All reactions involving ions are reversible. In the displacements discussed in the preceding chapter, the reversibility is rarely of practical importance because equilibrium is usually attained when the reaction has proceeded almost to completion in one direction or the other. In general also, changes in temperature and in external pressure have little effect on the equilibrium in ionic reactions. But changes in concentration of the components of the system play a most important rôle, and must therefore be taken up in detail.

The Ionization of Weak Electrolytes.—When a weak electrolyte is dissolved in an ionizing medium, a condition of equilibrium is set up between the un-ionized molecules and the ions. The concentration of these components is determined by the strength of the electrolyte and by the concentration of the solution, as has already been discussed (see page 200). After the attainment of equilibrium, the **removal** or **addition** of any component shifts the equilibrium according to Le Chatelier's rule.

The effects outlined above may be illustrated in the case of the rather slightly ionized acetic acid. When dissolved in water, it dissociates to a limited extent according to the equation:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-.$$

The addition of either acetate or hydrogen ions to the solution must drive the reaction to the left in order that the system may, by removing the added material, undo the stress to which it has been subjected. Sodium acetate, for example, is a highly

ionized salt. If added to a solution of acetic acid, it greatly increases the concentration of acetate ions. Some of these must, as just described, unite with some of the hydrogen ions to form more un-ionized acetic acid. But the acid properties of acetic acid are due to its hydrogen ions, and if they are partially removed, the acidity of the solution must be reduced by the addition of the sodium acetate. Hydrogen ions turn the color of aqueous solution of methyl orange from brownish yellow to red. Acetic acid, by virtue of the hydrogen ions it furnishes, of course, does the same. But the addition of sodium acetate to acetic acid destroys this property, because it so nearly completely reverses the ionization of the acid.

Addition of hydrogen ion to acetic acid must likewise drive the equilibrium between acetic acid and its ions to the left (in terms of the equation written above). The correctness of this conclusion may also be demonstrated by a simple test. Aqueous solutions of all highly ionized acetates give a precipitate of silver acetate when treated with silver nitrate. The reaction is, therefore, a test for the presence of acetate ion. But if nitric acid, which furnishes a high concentration of hydrogen ions, is added to the solution of sodium acetate before it is mixed with silver nitrate the precipitate fails to appear.

According to Le Chatelier's rule, removal of either hydrogen ions or acetate ions from the solution drives the reaction to the right, that is, to the further decomposition of acetic acid into its ions. When sodium hydroxide is added to acetic acid, the hydrogen ions of the latter react with the hydroxide ions of the former to give water which is only slightly ionized. Although a solution of acetic acid contains only a relatively small number of hydrogen ions at any one time, all of the acetic acid is used up in the reaction because, as the hydrogen ions are removed to form water, more acetic acid ionizes.

Another interesting instance of the effect of the removal of an ion is the reaction of sodium upon water. Water itself is slightly ionized according to the equation:

$$HOH \rightleftarrows H^+ + OH^-$$

Sodium removes hydrogen ion by displacement and is itself

converted into sodium ion.[1] As a result of the removal of hydrogen ion, the reaction represented by the equation proceeds to the right. Since the hydrogen ions thus formed are continuously removed, the hydroxide ions accumulate, and the resulting solution is a strong base. The complete change is given by the equation:

$$2Na + 2HOH \rightarrow 2Na^+ + 2OH^- + H_2$$ [2]

The addition or removal of common ions to solutions of weak electrolytes produces results analogous to those described in the case of acetic acid and water. This fact is frequently used in analytical chemistry to produce solutions containing definite concentrations of particular ions, but further elaboration of these applications is beyond the scope of this text. In the case of strong electrolytes, the common ion effect, as it is called, is of little importance because such electrolytes are practically 100 per cent ionized irrespective of the concentration of ions or molecules. The formation of slightly soluble substances is a special case and is discussed below.

Equilibrium Relations, in Ionic Double Decompositions.—The application of Le Chatelier's rule to ionic double decompositions is not a simple matter because of the large number of components involved. The difficulty may be avoided by restating the rule in the following modified form: **IONIC DOUBLE DECOMPOSITIONS ALWAYS PROCEED IN THE DIRECTION IN WHICH THE CONCENTRATIONS OF IONS DECREASE.** The concentration of ions may be decreased by (1) the formation of an insoluble substance, (2) the formation of a slightly ionized substance, (3) the formation of a complex ion, (4) the discharge or change in the charge of an ion. Illustrations of the last named methods for removing ions have been encountered in the discussions of displacement and of oxidation and reduction. The third will be taken up later when complex ions are studied in more detail.

[1] See page 214.

[2] In this equation the molecular formulae of slightly ionized substances like water and the ionic formulae of highly ionized substances like sodium hydroxide are used. This procedure gives a clear picture of the reaction, and will be employed extensively in the text.

The first two are by far the most important, and are illustrated in the following paragraphs.

Removal of Ions by the Formation of an Insoluble Substance. —Complete insolubility is probably only a theoretical possibility. But there are substances which are so slightly soluble that they are almost completely removed from the solution by precipitation or by volatilization. If they are removed, the double decomposition in which they are formed goes practically to completion. The reaction between barium chloride and sulfuric acid and that between sodium chloride and silver nitrate are but two of innumerable illustrations which might be cited. In the following equations, the insoluble substances, the precipitation of which drives the reaction to completion, are indicated by the sign ↓, and the direction of the reaction is indicated by a long arrow.[1]

$$BaCl_2 + H_2SO_4 \rightleftharpoons 2HCl + BaSO_4 \downarrow$$

$$AgNO_3 + NaCl \rightleftharpoons AgCl \downarrow + NaNO_3$$

If an appreciable amount of the slightly soluble substance remains in solution, the reaction does not go to completion. The actual point of equilibrium can then be determined only when the solubility of the substance in question is accurately known.

Cases are frequently encountered in which there are two slightly soluble substances. The precipitation of one tends to draw the raction in one direction and that of the other to draw the reaction in the opposite direction. In such a case the less soluble precipitate exerts the determining effect. Here also, exact knowledge of the relative solubilities is necessary in order to foretell accurately the position of the point of equilibrium. Silver chloride is less soluble than silver chromate although neither is very soluble in water; the reaction:

$$\underset{\text{Red-brown}}{Ag_2CrO_4 \downarrow} + 2NaCl \rightleftharpoons \underset{\text{White}}{2AgCl \downarrow} + Na_2CrO_4$$

[1] Evidently, since the reactions are ionic, any substances yielding barium ion and any one yielding sulfate ion could have been substituted for those chosen. In the second illustration, any silver salt and any chloride might have been used.

goes chiefly in the direction indicated by the longer arrow as is clearly shown by the accompanying color change.

The effects of solubility upon equilibrium in ionic decompositions account for the changes which occur during the evaporation of a mixture of 2 ionogens incapable of reacting to form either very insoluble or slightly ionized substances. When the mixture is prepared, no decided reaction occurs. For example, take a mixture of very dilute solutions of silver nitrate and potassium permanganate. The only possible reaction is a double decomposition leading to the formation of silver permanganate and potassium nitrate according to the equation:

$$AgNO_3 + KMnO_4 \rightarrow AgMnO_4 + KNO_3$$

But if the equation is written according to the theory of ionization (bearing in mind that all of the components of the system are highly ionized), the result is:

$$Ag^+ + NO_3^- + K^+ + MnO_4^- \rightleftarrows Ag^+ + MnO_4^- + K^+ + NO_3^-$$

No change of any sort is involved in the reaction, and therefore the latter cannot be said to proceed either to the right or to the left. But if the solution is gradually evaporated, it must ultimately become saturated with one or the other of the four possible components. The least soluble of the four is silver permanganate. After evaporation has proceeded beyond the point of saturation of the solution with this component, the silver permanganate precipitates, and the reaction proceeds to the right. But it is impossible to make the reaction go to completion in this direction even by complete evaporation. After the removal of more water, the solution becomes saturated also with potassium permanganate. Further removal of water then causes precipitation of both silver and potassium permanganates, and the equilibrium point remains unchanged.

Removal of Ions by the Formation of a Slightly Ionized Substance. I. Displacement of a Weak Acid from its Salts by Strong Acids.—One of the characteristics of strong acids is their ability to displace weak acids from the salts of the latter. When hydrochloric acid is mixed with sodium acetate, acetic acid and sodium

chloride are formed. This reaction is called displacement of acetic acid. The reverse action proceeds only to a very slight extent. The equation is:

$$Na^+ + C_2H_3O_2^- + H^+ + Cl^- \rightleftharpoons Na^+ + Cl^- + HC_2H_3O_2$$

because all of the substances except acetic acid are highly ionized. Evidently hydrogen and acetate ions are removed at the right. According to the modified Le Chatelier's rule the reaction proceeds in that direction. But acetic acid is by no means completely un-ionized—the hydrogen and acetate ions are consequently by no means completely removed, and the reaction does not go to completion. If (in place of sodium acetate) sodium cyanide had been used, the reaction:

$$Na^+ + CN^- + H^+ + Cl^- \rightleftharpoons Na^+ + Cl^- + HCN$$

would have occurred. Hydrocyanic (or prussic) acid is much less ionized than is acetic acid. The removal of the hydrogen and cyanide ions is much more complete in this case than was the removal of hydrogen and acetate ions in the preceding one, and the reaction therefore proceeds much more nearly to the complete displacement of the hydrocyanic acid. When acetic acid is added to sodium cyanide the following reaction occurs:

$$Na^+ + CN^- + HC_2H_3O_2 \rightleftharpoons Na^+ + C_2H_3O_2^- + HCN$$

Reaction to the left is favored by removal of hydrogen and acetate ions, while reaction to the right is favored by removal of hydrogen and cyanide ions. The removal of the ions at the right is far more nearly complete than at the left. The reaction therefore proceeds more to the right than to the left, but obviously an equilibrium must be attained in which appreciable quantities of each acid are left. Accurate study of concentrations at equilibrium in such reactions is one of the chemical means of determining relative strengths of acids.

Since the preceding discussion involved the substances of the reactions only incidentally, and dealt exclusively with the relative degree of ionization, it follows that the same sort of

reasoning applies to bases—that is, **strong bases displace weak bases from their salts.** Simple illustrations of this case are not common because most of the weaker inorganic bases are also slightly soluble. One illustration is cited in Exercise 7, at the close of the chapter.

Removal of Ions by the Formation of a Slightly Ionized Substance. II. Neutralization.—Sodium hydroxide reacts with hydrochloric acid to form water and sodium chloride. All of the substances involved, with the exception of water, are highly ionized, and the equation is therefore:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + HOH$$

The degree of ionization of water is extremely small. Consequently there is a very large decrease in the concentration of the hydroxide and hydrogen ions as the reaction proceeds to the right. On the other hand, the acid and the base are just as highly ionized as sodium chloride, and reaction to the left is therefore attended by no decrease in concentration of ions. The large decrease of the concentrations of ions to the right tends strongly to draw the reaction in that direction; there is no corresponding "pull" [1] toward the left. The reaction therefore goes to completion to the right. The sodium and the chloride ions are obviously without influence in determining the course of the reaction. The only determining factor is the degree of ionization of water and of the other components. Consequently, if the formulae of the substances which undergo no change (Na^+ and Cl^-) are left out of the equation, the latter is applicable to the reaction between any strong base and any strong acid.

$$H^+ + OH^- \rightleftharpoons HOH$$

That neutralization of strong bases by strong acids is nothing more than reaction between hydrogen and hydroxide ions is

[1] The terms "pull" and "drive" and "draw" used in this connection are, like most analogies, quite inaccurate. The removal of ions does not "pull" or "drive" or "draw" the reaction to the left or right. It merely **allows the reaction to proceed in one particular direction or the other.** The term is nevertheless used frequently in the text because it has been found helpful to students.

seen from the fact that the heat of neutralization in all such reactions is identical—in other words the heat of the reaction between hydroxide and hydrogen ions.

When a **weak base** is neutralized by a **strong acid** or **a strong base** by a **weak acid,** the heat of neutralization is not the same as it is in neutralization reactions in which both acid and base are strong. The addition of a strong base to a weak acid first causes the hydrogen ions present in the solution of the acid to unite with hydroxide ions to form water. The removal of the hydrogen ions causes the weak acid to ionize further (see page 223), until all of the acid is dissociated. In the process of dissociation heat is given out or absorbed, and this quantity of heat must be added to or subtracted from the heat of union of hydroxide and hydrogen ions. In the same way the difference in the heat of reaction between weak bases and strong acids, and that of a reaction in which both are strong is accounted for.

Removal of Ions by Formation of a Slightly Ionized Substance. III. Hydrolysis.—Hydrolysis, as the term is used in inorganic chemistry, is the reaction between a salt and water to form a base and an acid. If the base is designated by BOH, the acid by HA, and the salt by BA, the equation is:

$$BOH + HA \rightleftarrows BA + HOH.$$

The reaction toward the right is called **neutralization** and the reaction to the left **hydrolysis.** The one reaction is the reverse of the other. In the last section it was shown that when the base and the acid are both highly ionized there is no tendency whatever for hydrolysis to occur—in other words, **salts derived from strong bases and strong acids are not hydrolyzed.**[1] An aqueous solution of such a salt therefore contains no more hydrogen ions and hydroxide ions than are furnished by the ionization of water—the solution is **neutral.** Such a solution can be formed either by dissolving the salt in water, or by mixing equivalent quantities of a strong base and a strong acid.

The situation is somewhat different if either the acid or the

[1] Experimental illustrations of hydrolysis are mentioned in connection with indicators, page 238.

base used is not highly ionized. For a full understanding of this case several instances must be discussed in detail. The reaction between acetic acid and sodium hydroxide may be chosen as an illustration of the **neutralization of a weak acid by a strong base.** This discussion will also deal with the **hydrolysis of the salt of a strong base and a weak acid,** since the two names refer merely to opposite directions of the same reversible reaction. In the equation for the reaction the molecular formulae for the slightly ionized substances and the ionic formulae of the highly ionized substances may be used:

$$HC_2H_3O_2 + Na^+ + OH^- \rightleftharpoons Na^+ + C_2H_3O_2^- + HOH$$

As the reaction proceeds to the right, the concentration of the hydroxide ion decreases from that furnished by sodium hydroxide to that furnished by water,—a very great decrease since the base is practically 100 per cent ionized and water hardly at all. The concentration of hydrogen ion also decreases. But the decrease is much smaller, since acetic acid which furnishes the hydrogen ion on the left is not very highly ionized, even though its degree of ionization is considerably greater than that of water. As the reaction proceeds to the left, there is a decrease in the concentration of the acetate ion from that furnished by highly ionized sodium acetate to that furnished by slightly ionized acetic acid. The decrease in concentration of the acetate ion is very much smaller than the decrease of hydroxide ion when the reaction goes in the opposite direction. The large decrease in the concentration of the hydroxide ion and the smaller decrease in the concentration of the hydrogen ion both tend to draw the reaction to the right; the small decrease in the concentration of the acetate ion tends to draw the reaction to the left. As a result the reaction does not go to completion in either direction. Since the " pull " toward the right is so very much greater than that to the left, equilibrium must be attained when the reaction has gone **very nearly** to completion toward the right.[1]

The same condition of equilibrium is reached by starting

[1] A scheme for noting the various factors which affect hydrolysis is suggested in Exercise 4 at the close of this Chapter.

either with sodium acetate and water, or with sodium hydroxide and acetic acid. Hence, the discussion may be summarized by saying that when equivalent amounts of acetic acid and sodium hydroxide are mixed, or when sodium acetate is dissolved in water, the solution at equilibrium contains only a very small amount of acid and base. Since the acid is less ionized than the base, the solution contains more hydroxide ions than hydrogen ions—it is therefore not neutral, but very slightly basic.

In the preceding discussion the only property considered was the degree of ionization. Hence the same conclusions must be reached with regard to the action of any weak acid on any strong base. The conclusions drawn in the particular instance may therefore be generalized as follows: **Aqueous solutions of salts of moderately weak acids and strong bases are slightly hydrolyzed, and give a slightly basic reaction.** Or, solutions produced by mixing equivalent quantities of moderately weak acids and strong bases are slightly basic.[1]

Had a very weak acid, like hydrocyanic acid, been used in place of the moderately weak acetic acid the condition at equilibrium would have been only slightly different, as is evident from the equation:

$$HCN + Na^+ + OH^- \rightleftharpoons Na^+ + CN^- + HOH$$

Toward the right, the decrease in concentration of hydroxide ion is the same as in the preceding case. The decrease in hydrogen ion concentration is even smaller than when acetic acid is used, because hydrocyanic acid is not much more ionized than water. The tendency of the reaction to proceed to the right is therefore slightly less than in the case of acetic acid. On the other hand, the decrease in concentration of cyanide ion, as the reaction proceeds in the opposite direction, is somewhat greater than the corresponding decrease in acetate ion concentration, and the "pull" to the left is therefore somewhat greater. But the factors drawing the reaction to the right are still considerably greater than those drawing it to the left, and the reaction still

[1] The terms "slightly basic" in reaction refers to the slight excess of hydroxide ion shown to be present in the solutions. It will be further discussed in the section on Acidimetry and Indicators, pages 235–238.

goes chiefly in the former direction, though not so far as in the preceding case. Whether the reaction begins with equivalent amounts of hydrocyanic acid and base, or with sodium cyanide and water, a small amount of sodium hydroxide and of hydrocyanic acid will be left in the solution at equilibrium. In this case, however, the base is very much more highly ionized than the acid, and there is a very decided excess of hydroxide ion. The solution is therefore decidedly basic.

Again the discussion involved only a consideration of the degree of ionization of the various substances taking part in the reaction. Hence the following generalized statement is permissible: **Aqueous solutions of salts of very weak acids and of strong bases are somewhat hydrolyzed, and give a decidedly basic reaction.** Or, solutions produced by mixing equivalent quantities of very weak acids and strong bases are decidedly basic.

By employing the type of reasoning just illustrated, the student should prove for himself the correctness of the following statements:

Aqueous solutions of salts of moderately weak bases and of strong acids are slightly hydrolyzed, and give a slightly acid reaction. Or, solutions produced by mixing equivalent quantities of moderately weak bases and of strong acids are slightly acid. And: **Aqueous solutions of salts of very weak bases and strong acids are somewhat hydrolyzed, and give a decidedly acid reaction.** Or, solutions produced by mixing equivalent quantities of very weak bases and strong acids are decidedly acid.

The last case to be discussed is the reaction between a weak base and a weak acid, for which ammonium hydroxide and hydrocyanic acid are chosen as illustrations. The equation is:

$$NH_4OH + HCN \rightleftarrows NH_4^+ + CN^- + HOH$$

In the action toward the right, neither the decrease in the concentration of hydrogen or hydroxide ions is as great as when the acid and base are strong. The tendency of the reaction to go to the right is therefore smaller than in any of the previous cases. On the other hand, the concentrations of both cyanide and ammonium ions decrease as the reaction goes to the left.

The factors drawing the reaction to the left are thus much greater than in any of the preceding cases. Hydrolysis must, on this account, be very much more extensive, and neutralization much less complete for a weak acid and a weak base than when either base or acid are strong. In general, **aqueous solutions of salts of weak bases and of weak acids are extensively hydrolyzed.** In the particular case under discussion, the base is appreciably stronger than the acid, and the resulting solution is alkaline, but that need not always be true. The acid in many instances is stronger than the base, or the two may be of approximately equal strength. Consequently no general statement can be made about acidity or basicity of the salt of a weak acid and a weak base.

Even when the acid and base both are weak hydrolysis is not complete. Complete hydrolysis of a salt (unless complicating factors such as the formation of insoluble substances enter into consideration) must indicate extremely minute ionization of the corresponding base or acid.

From the foregoing discussions, it is clear that neutralization takes place because water is hardly ionized at all, and that hydrolysis occurs because, in spite of the slight ionization of water, the latter nevertheless furnishes a few hydrogen and hydroxide ions. Consequently, rise in temperature, which greatly increases the degree of ionization of water, must greatly increase the hydrolysis of salts. Likewise, the presence of an excess of water favors hydrolysis; salts of weak bases or of weak acids are more extensively hydrolyzed in dilute than in concentrated solutions.[1] On the other hand, hydrolysis can be prevented or decreased by the addition of an excess of a base or an acid, as is to be expected from Le Chatelier's rule.

The Actual Degree of Hydrolysis of Salts of Various Acids and Bases.—Thus far the degree of hydrolysis has been spoken of in relative terms only. Although the methods of calculating these quantities or of determining them by experiment are beyond the scope of this text, it is desirable to have some idea of the extent

[1] The degree of hydrolysis of salts derived from acids and bases, both of which are weak, is not so greatly affected by dilution, as it is in the cases in which either base or acid is strong. The reason cannot be discussed here.

to which reactions of this type proceed in various cases. Students generally overestimate the degree of hydrolysis, which is usually small in moderately dilute solutions if either the base or the acid is highly ionized. The following table illustrates this point. In the first column are given the name of the salt and its formula. In the case of salts of dibasic acids, the reaction for which the percentage of hydrolysis is given is indicated by the formula of the compound produced. Thus sodium carbonate reacts with water to give sodium bicarbonate and sodium hydroxide according to the equation: $Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH$. Water reacts further with the bicarbonate to give carbonic acid and sodium hydroxide: $NaHCO_3 + H_2O \rightleftarrows H_2CO_3 + NaOH$. The

TABLE XI

THE APPROXIMATE PER CENT OF HYDROLYSIS OF VARIOUS SALTS IN AQUEOUS SOLUTION AT 25°

Salt		Per cent Hydrolyzed N/1 Solution	Per cent Hydrolyzed N/10 Solution
Sodium bisulfite	$NaHSO_3 \rightarrow H_2SO_3$	Practically 0	Practically 0
Sodium sulfite	$Na_2SO_3 \rightarrow NaHSO_3$	0.004	0.005
Sodium nitrite	$NaNO_2$	0.0005	0.0016
Sodium acetate	$NaC_2H_3O_2$	0.003	0.007
Primary sodium phosphate	$NaH_2PO_4 \rightarrow H_3PO_4$	Practically 0	Practically 0
Secondary sodium phosphate	$Na_2HPO \rightarrow NaH_2PO_4$	0.015	0.04
Tertiary sodium phosphate	$Na_3PO_4 \rightarrow Na_2HPO_4$	3.0	17
Sodium bicarbonate	$NaHCO_3 \rightarrow H_2CO_3$	0.02	0.06
Sodium carbonate	$Na_2CO_3 \rightarrow NaHCO_3$	1.3	4.0
Sodium cyanide	$NaCN$	0.5	1.4
Sodium bisulfide	$NaHS \rightarrow H_2S$	0.03	0.1
Sodium sulfide	$Na_2S \rightarrow NaHS$	90	Almost complete
Ammonium bicarbonate	$NH_4HCO_3 \rightarrow H_2CO_3$	25	
Ammonium cyanide	NH_4CN	40	

statement in the table with regard to sodium carbonate is: sodium carbonate, $Na_2CO_3 \rightleftarrows NaHCO_3$. This indicates that the per cent of hydrolysis given refers to the first of the reactions mentioned above.

The student should not attempt to learn tables of this sort by heart, but should use them as illustrations of the text. He should note that most of the sodium salts mentioned are hydrolyzed to less than 1 per cent, although the salt of the very weak acid, HCN, is included. This is due to the fact that sodium hydroxide is a strong base. On the other hand the ammonium salts of the weak acids are very much more extensively hydrolyzed because they are each derived from a base and an acid, both of which are weak. He should note further that among the salts of di- or tribasic acids, those formed by neutralizing only one of the hydrogen ions are much less hydrolyzed than those formed by neutralizing two of the hydrogen ions, and that the salts formed by neutralizing a third hydrogen ion, as in phosphoric acid, are still more hydrolyzed. This is an illustration of the fact that the first hydrogen ion is dissociated from such acids the most readily, and that each successive hydrogen ion is less easily dissociated than the preceding one. The case of the acid, hydrogen sulfide, is particularly noteworthy. Sodium bisulfide, the salt formed by neutralizing only one of the hydrogen ions with sodium hydroxide, is hydrolyzed to the extent of only 0.1 per cent in N/10 solution. Sodium sulfide, the salt formed by neutralizing both of the hydrogen ions of hydrogen sulfide, is almost completely hydrolyzed. This is due to the fact that the ionization of hydrogen sulfide into the first hydrogen ion is much more extensive than that of water, while the degree of dissociation into the second hydrogen ion is less than that of water. Finally attention is called to the fact that the salts of strong bases and of weak acids are more hydrolyzed in the more dilute solutions. Similar relations would of course be exhibited by salts of weak bases and strong acids. Questions 10 and 11 are helpful in studying this table.

Standard Solutions. Titration, Acidimetry, Indicators.—The problem of determining the amount of some definite substance in a given solution is frequently encountered in chemical work.

To solve the problem, **standard solutions** are employed. A standard solution is one which contains an accurately known number of gram equivalents (see page 130) per liter—usually 1, 0.1 or 0.01 gram equivalent. The standard solution chosen for any given analysis must contain a substance which reacts with the substance to be analyzed. The standard solution is added drop by drop to the unknown solution until the resulting mixture contains equivalent quantities of the two substances. Suppose, for example, that the unknown solution contains sulfuric acid. A base, such a sodium hydroxide, is chosen as the standard solution. Let us say that 50 c.c. of the latter have to be added to 10 c.c. of the unknown before base and acid are present in equivalent amounts. We know then that the number of gram equivalents of sulfuric acid contained in 10 c.c. of the unknown solution is the same as the number of gram equivalents of base contained in 50 c.c. of the standard solution. If the latter is N/10, 50 c.c. contains $\frac{1}{20}$ of the amount contained per liter or $\frac{1}{200}$ of a gram equivalent. Since 10 c.c. of the acid have been found to contain this same amount, 1 liter of the acid contains $\frac{1}{2}$ of a gram equivalent of sulfuric acid. The acid solution is therefore $\frac{1}{2}$ normal, and contains 24.519 grams of sulfuric acid per liter. Adding equivalent quantities of substances in solution to each other for purposes of analysis is called a **titration**; when the solutions contain acids or bases, the special name, acidimetry, is sometimes used.

In order to be able to carry out a titration, the chemist must have some means of determining when the two substances are present in equivalent amounts. Formation of precipitates and, more commonly, color changes are employed. A substance which changes color when equivalent amounts of the reagents, particularly acids and bases, have been mixed is called an **indicator.** The use of indicators may be understood most readily if the changes that occur on adding a base to an acid, or *vice versa*, are once more reviewed. Suppose hydrochloric acid is added to a solution of sodium hydroxide. The concentration of hydroxide ion gradually decreases until the amount of acid added is just equivalent to the amount of base originally present—at that moment hydrogen ions and hydroxide ions have the con-

centration they have in pure water, i.e., 10^{-7} gram equivalent of each per liter. The addition of another drop of acid produces a considerable increase in the concentration of hydrogen ion, while if addition of acid had ceased just before this point of equivalence was reached, there would have been quite a considerable excess of hydroxide ion because both acid and base are strong. Any substance the color of which changes when the concentration of hydroxide ion or of hydrogen ion is not far from that of pure water may be used as indicator for the reaction. All of the commonly used indicators such as methyl orange, phenolphthaleïn or litmus have this property.

If a **weak base is to be titrated** against a strong acid, it must be remembered that solutions containing equivalent amounts of a weak base and of a strong acid are slightly acid in reaction. (See page 232.) Consequently, the indicator to be used for such a titration should be one which changes color when there is a slight excess of hydrogen ion in the solution. Methyl orange, for instance, turns from yellow to red when the concentration of hydrogen ion is 10^{-5}—that is when there is more hydrogen ion than there is in pure water—and may therefore be used for the titration of weak bases. On the other hand, solutions containing equivalent amounts of a weak acid and a strong base are slightly basic in reaction, and the indicator should change color when there is an excess of hydroxide ion present. Phenolphthaleïn changes from colorless to red when the concentration of hydroxide ion is 10^{-6} and may therefore be used in the titration of weak acids. Very weak acids or very weak bases cannot conveniently be titrated by these methods.[1]

Since solutions containing equivalent amounts of acid and base can be prepared by dissolving the corresponding salt in water, the reactions of such solutions may easily be demonstrated. For example a solution of sodium chloride in water

[1] Since acids and bases vary from weak to strong with all intermediate strengths, a series of indicators whose color changes occur at various hydrogen ion or hydroxide ion concentration is very useful. Such indicator series are known. Their description and details of their use will be found in modern books on volumetric analysis or physical chemistry. (See references.)

is neutral to indicators; a solution of sodium acetate is alkaline, and a solution of ferric chloride is acid.

Removal of Ions. IV. Solution of Slightly Soluble Salts of Weak Acids by Strong Acids.—Just as the formation of more than one insoluble substance or of more than one slightly ionized electrolyte may tend to draw the reaction in question in both directions, so the effect of an insoluble substance and of a slightly ionized one may counteract one another in the same reaction. This may be illustrated in the case of the solution of calcium oxalate (CaC_2O_4) by hydrochloric acid. The equilibrium between calcium oxalate and its ions may be formulated by the equation:[1]

$$CaC_2O_4 \downarrow \rightleftarrows Ca^{++} + C_2O_4^{=}$$

Under ordinary conditions, the equilibrium is displaced far to the left because the slightly soluble calcium oxalate precipitates, thus removing calcium and oxalate ions. But when hydrochloric acid is added to the solution, its hydrogen ions tend to unite with the oxalate ions to form the new ion, $HC_2O_4^-$, which is very little dissociated into H^- and $C_2O_4^{=}$. In this way oxalate ions are removed, and the reaction is drawn to the right. If enough hydrochloric acid is used the reaction can be driven to completion in that direction, and the solid calcium oxalate entirely disappears.[2] That there really is a counteraction of two opposing tendencies may be shown by the fact that calcium oxalate is not dissolved by acetic acid. Acetic acid ionizes so slightly that it does not furnish enough hydrogen ion to drive the reaction to the right against the influence of the slight solubility of calcium oxalate. Another way of showing the importance of the two influences is to compare the behavior of calcium carbonate with that of calcium oxalate. The equation for the carbonate is:

$$CaCO_3 \downarrow \rightleftarrows Ca^{++} + CO_3^{=}$$

[1] The question of the existence of molecules in the case of highly ionized substances has not yet been definitely settled. The use of this method of formulation is allowable as a matter of convenience.

[2] The complete equation is:

$$2CaC_2O_4 + 2HCl \rightarrow Ca(HC_2O_4)_2 + CaCl_2.$$

Calcium carbonate is soluble both in hydrochloric and in acetic acid. Carbonic acid (H_2CO_3) is so slightly ionized that even acetic acid furnishes enough hydrogen ions to remove the carbonate ions from the solution, and thus to drive the reaction to the right.

The Usefulness of the Theory of Ionization.—This chapter has shown the usefulness of the theory of ionization in explaining a great variety of reactions, and in broadening the chemist's grasp of the principles underlying many chemical changes. One very great simplification brought about by the ionic theory has as yet been touched on only by implication. Reactions of highly ionized substances are essentially those of the ions.[1] Consequently the behavior of the ions alone need be studied, particularly in the case of salts all of which are strong electrolytes. Suppose that the chemist has learned the properties of 5 positive and 5 negative ions other than hydrogen and hydroxide ions—he then can foretell the properties of the 25 salts of which these ions may be constituents.

Nature of Ionic Properties.—The simplicity of ionic reactions becomes even greater when it is remembered that ions undergo only very few types of reaction. The following is a practically complete list of what may happen to simple ions:[2] (1) they may lose their charge or (2) change their charge; they may unite to form (3) insoluble substances or (4) slightly ionized substances, and (5) they may form complex ions. (1) and (2) have been discussed under oxidation and reduction. In a later chapter it will be shown that the ease with which simple ions lose their charge is related to the atomic weight of the corresponding element—a fact which introduces further simplification. In considering the fourth item, one important fact must be borne in mind. Students very commonly make the mistake of believing

[1] The fact that most salts and other highly ionized electrolytes display no properties which can be definitely ascribed to the molecules has been used as an argument in favor of the theory that such electrolytes are 100 per cent ionized under all conditions. It is possible that non-ionic reactions are not discoverable because the ionic reactions are so very much more rapid or because the ionizing solvent represses the action of the un-ionized molecules.

[2] Simple ions are those formed directly by the loss or gain of electrons by atoms. Ions, like $SO_4^{=}$, NO_3^{-}, are called compound ions.

that positive ions and negative ions always tend to unite with one another. As a matter of fact, **ions, with the exception of hydrogen or hydroxide ion, have very little tendency to form molecules,** as is shown by the fact that practically all salts are highly ionized. Consequently, the possibility of the formation of slightly ionized substances need be considered only when acids or bases can be products of the reactions. The reactions between non-ionized substances, to which most of the organic compounds belong, cannot be reduced to such a small list, and cannot be so simply classified.

The Effect of the Solvent on Ionic Reactions.—Very few of the common solvents other than water possess the property of ionizing dissolved substances extensively. Consequently not much is known of the effect of the solvent on ionic reactions. The behavior of solutes in **liquid ammonia** is of interest. Solubility is known to be affected greatly by the nature of the solvent. Since solubility has a decided influence in determining the direction of ionic double decompositions, the solvent through its effect on solubility may affect such reactions. For example, silver chloride is very insoluble in water and very soluble in liquid ammonia; barium chloride is fairly soluble in water but very insoluble in liquid ammonia. Consequently the reaction:

$$2AgNO_3 + BaCl_2 \rightleftarrows 2AgCl + Ba(NO_3)_2$$

goes completely to the right in aqueous solution, and completely to the left in liquid ammonia.

The following illustration of the influence of solvents is important in showing that many of our definitions are based on the accident that, in our section of the universe, water is the common solvent. An acid is a substance which yields hydrogen ions. The most characteristic property of a base is that it neutralizes acids. As has been shown, substances yielding the hydroxide ion do this because, in aqueous solutions, they unite with hydrogen ion to form water, which is the least ionized electrolyte in aqueous solutions. Liquid ammonia, on the other hand is ionized according to the equation:

$$NH_3 \rightleftharpoons NH_2^- + H^+$$

The ionization of ammonia, like that of water, is extremely minute. Consequently, in liquid ammonia, NH_2^-, unites with hydrogen ion, thus removing the latter from solutions. Any substance yielding the NH_2^- ion would be considered a base in this solvent. Actually sodium amide ($NaNH_2$) and potassium amide (KNH_2) act just as do the hydroxides of these metals in aqueous solutions. It is clear from these illustrations that the effect of the solvent on ionic reactions is an important and fascinating subject—unfortunately its elaboration cannot be undertaken in this text.

EXERCISES

(1) Explain why the weak acid, HCN, is even less ionized in solutions containing potassium cyanide than it is in pure water. Why is it less ionized in solutions of acids such as hydrochloric than it is in pure water?

(2) (*a*) Write the reaction between sodium carbonate and hydrochloric acid in such a way that highly ionized substances are represented by the formulae of their ions and slightly ionized ones by the formulae of the molecules. (*b*) Explain why the reaction goes nearly to completion even in solutions so dilute that no carbonic acid escapes as CO_2. (*c*) Show why the escape of CO_2 in more concentrated solutions or at higher temperatures favors completion of the reaction.

(3) Judging by the relative degrees of ionization (see table on page 202) in which direction would the following reaction tend to go:

$$Na_2CO_3 + H_2S \rightleftarrows Na_2S + H_2CO_3?$$

In answering, formulate the reaction as has been done in the text and as described in question (2). Give reasons for your answer. Mention each factor which tends to draw the reaction in one or the other direction. Is the reaction complete in either direction?

(4) Explain why the salt, potassium cyanide, is partially hydrolyzed in aqueous solution. An excellent procedure is to write the equation according to the method used in problems (2) and (3) and in the text, and then to write under the equation a list of the ions involved. Opposite the symbol of each ion, place an arrow indicating the direction in which the reaction is accompanied by decrease in the concentration of that ion. If there is no decrease, make a zero in place of the arrow; if the decrease is great make a long arrow; if small, a short arrow. Sum up all the arrows

to indicate the direction in which the tendency for the reaction to proceed is the greatest.

(5) Answer as in (4) for the salt, potassium acetate. By comparing the lengths of the various arrows written down for each ion in the two cases, judge which salt, potassium cyanide or potassium acetate is more hydrolyzed.

(6) State which of the following salts gives a neutral, which an acid, which a strongly acid, which a basic and which a strongly basic reaction towards indicators in aqueous solution: sodium borate, sodium iodide, potassium acetate, copper sulfate, aluminium chloride, nickel sulfate, silver nitrate, ammonium chloride. (In drawing your conclusions use the table on page 201.)

(7) Explain why the addition of sodium hydroxide to a solution of ammonium chloride liberates ammonium hydroxide.

(8) Explain why sodium carbonate may be used to neutralize a strong acid.

(9) Will approximately equal quantities or greatly differing quantities of a normal solution of sodium hydroxide be required to neutralize normal solutions of acetic and of hydrochloric acids? In answering, consider carefully the statement on page 223, second paragraph.

(10) (*a*) Which of the monobasic acids, the salts of which are mentioned in the table on hydrolysis of salts (page 234) is the weakest and which the strongest acid? (*b*) What is the evidence in this table to show that sodium hydroxide is a stronger base than ammonium hydroxide?

(11) (*a*) Write the equations for the reactions to which the per cent of ionization, given in the table, page 201, refers. (*b*) How much hydroxide ion, expressed in terms of gram molecular weights of OH^- per liter, is present in N/10 solution of the following salts: sodium acetate, sodium bicarbonate, sodium cyanide, sodium sulfide? Assume that sodium hydroxide is 100 per cent ionized and use the data of the table, page 234.

REFERENCES

Hildebrand—Principles of Chemistry, Chapter XIII.

Stieglitz—Qualitative Chemical Analysis, Vol. I, is an excellent discussion of the theory of ionization and of the equilibrium relations of the ions and molecules. It is somewhat more advanced, and treats of equilibrium from the quantitative rather than the qualitative point of view presented in this text. Chapters IV, V and VI are of particular interest in connection with Chapters XIII, XIV, and XV of this text.

CHAPTER XVI

SULFUR.—ALLOTROPIC MODIFICATIONS.—HYDROGEN SULFIDE

Applications and Review of Equilibria in Ionic Reactions

Before taking up the remaining important theories discussed in this text, the properties of two of the most important elements, sulfur and nitrogen, will be studied. In so doing, opportunity is given to review the principles presented thus far, and to become more familiar with their applications.

Sulfur is widely distributed in nature both in the free condition and combined. In the free state it is frequently found on or near the surface of the earth in volcanic regions or near hot springs. For this reason the element has been known since very early times, in contrast to most of the other non-metallic elements which have been prepared only within the past two centuries. The sulfur deposits of Louisiana and Texas, which furnish a large part of the world's supply of the element, are of special interest because of the ingenious method devised for working them. The deposits are located below about 900 feet of rock, quicksand and clay. The expense of sinking shafts through this material and of mining the sulfur would make its cost prohibitive. The difficulty is avoided by taking advantage of the fact that sulfur has a relatively low melting point (114.5°). Water, heated to 170° under pressure, is pumped down to the deposit through pipes. A portion of the sulfur is thereby melted. The resulting liquid is heavier than water, but when compressed air is forced through it, bubbles of air attach themselves to the sulfur, and raise the latter to the surface in a return pipe.

Sulfur is found in combination with many elements. Many important ores such as galena (PbS), zinc blende (ZnS), and

copper and iron pyrites (Cu_2S and FeS_2) are sulfides. Large deposits of sulfates, such as barium and calcium sulfates, are known. So much free sulfur is found that it is not necessary to prepare the element from these compounds, but they are used to manufacture other important substances such as sulfuric acid and hydrogen sulfide. Sulfur in various compounds occurs also in living organisms and the element is unquestionably one of those without which the higher forms of life could not exist.

As native sulfur is usually contaminated with other substances, it is purified by distillation from iron retorts. The vapor is condensed in brick chambers. Before these have become thoroughly warmed, the sulfur condenses on the walls to fine crystals which are collected and sold as **flowers of sulfur.** When the chambers have become heated above the melting point of sulfur, the latter condenses into a liquid, and is run out into molds in which it solidifies. This material is known as **roll sulfur**. Flowers of sulfur and roll sulfur differ only in purity and in compactness; they are not different modifications of the element in the sense in which this term is used below.[1]

Solid Modifications of Sulfur.—When sulfur is very gradually heated, its temperature rises slowly to about 96°. At this point the temperature becomes constant, and an alteration in the crystalline form of the material occurs. The original crystals are **rhombic**; when heated above 96° they go over to a **monoclinic** variety. At the same time the density of the sulfur changes from that of rhombic sulfur, 2.06, to that of monoclinic, 1.96. As long as there is rhombic sulfur left the temperature remains constant, even though the mixture is gently heated,[2] but when

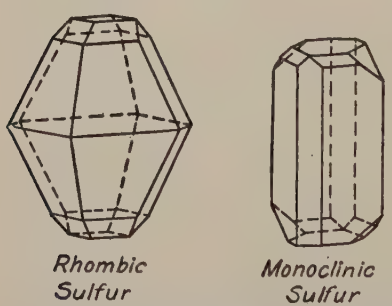


FIG. 8.—SULPHUR CRYSTALS SCHEMATICALLY REPRESENTED.

[1] Flowers of sulfur, as a result of the rapid cooling by which this product is obtained, contain considerable quantities of S_μ. (See below.)

[2] Too rapid heating causes super-heating in all such cases.

the rhombic sulfur has been completely transformed into the other variety further heating causes the temperature to rise. If, on the other hand, monoclinic sulfur is slowly cooled, the temperature drops to 96°, and there remains constant during the transformation into rhombic sulfur. The transformation is thus completely reversible. Application of Le Chatelier's rule (page 176) to the change indicates that heat is absorbed when rhombic sulfur is transformed into monoclinic, and that heat is liberated in the reverse change.

The phenomenon just described is quite similar to the freezing of water. The explanation of freezing, given in an earlier section of the text, is that lowering of temperature represents a decrease in the kinetic energy of the molecules. As a result, the attractive forces draw the molecules into so small a space that they have to orient themselves into a definite close-packed arrangement. Perhaps the arrangement of the sulfur molecules in the monoclinic variety is not the closest possible, and so, on further cooling, the molecules are forced to rearrange themselves to a still closer order.[1] Many elements and compounds exist in two forms, one of which is stable above and the other below a certain definite temperature, called the **transition temperature.** When the transformation occurs reversibly at a definite transition temperature, as in the case of sulfur, the substance is said to exist in **allotropic** modifications. When more than one modification but no definite temperature of reversible transformation exists, the substance is said to be **monotropic.** An illustration of this type is phosphorus, which is discussed in a later chapter.

Liquid Sulfur.—Further heating of monoclinic sulfur ultimately raises the temperature to the melting point. The resulting liquid is pale amber in color and quite mobile—i.e., it flows freely. But with continued rise in temperature, still another change is observed. The color darkens and the fluidity decreases until, at about 160°, the material is very dark red and so viscous that even if the containing vessel is inverted, the sulfur does not run out. Manifestly another modification of sulfur has been

[1] It should be mentioned that other hypotheses, involving the numbers or the arrangement of atoms in the molecules, have been advanced to explain the various solid modifications of substances. In some cases both factors may be operative. A thorough understanding of the causes which produce allotropic forms will come from the X-ray analysis of crystals (see p. 351).

formed. Above 260°, the liquid gradually becomes more fluid again. The yellow variety is called sulfur lambda (S_λ) and the dark red variety is known as sulfur mu (S_μ). Both are liquids, soluble in each other; for this reason there is no definite transition temperature. Ordinary liquid sulfur is a mixture of the two; as the temperature rises the proportion of S_μ increases, and as it falls the reverse change occurs.[1] S_λ and the two solid modifications of the element are soluble in carbon disulfide. Molecular weight determinations in this solvent show that each molecule of these varieties contains 8 atoms as indicated by the formula S_8. S_μ is insoluble in carbon disulfide and other solvents except S_λ.

The transformation of S_λ into S_μ and the reverse change are fairly slow. Consequently, the relative amounts of the two forms in liquid sulfur depend not only on the temperature, but also on the rate at which the liquid has been cooled or heated. If a sample of liquid sulfur is cooled very slowly from higher temperatures almost to the freezing point it contains relatively little S_μ, since there is time enough for the transformation of the latter into S_λ to reach the equilibrium state. If the cooling is rapid, the liquid near the freezing point is a solution of a relatively large amount of S_μ in S_λ, since, under these conditions, the time for transformation is too short to allow the mixture to reach equilibrium. Solutions, in general, have lower freezing points than the corresponding pure solvents; consequently when sulfur is rapidly cooled it shows a lower freezing point than when it is slowly cooled. But even a slowly cooled sample contains some S_μ in equilibrium with S_λ, and therefore freezes below the melting point of pure monoclinic sulfur. The freezing point of an equilibrium mixture of the two liquids is 114.5°; the melting point of pure monoclinic sulfur is 119.2°; that of pure rhombic sulfur is 112.8°. The last named value can be obtained only by heating the rhombic sulfur so rapidly that it has not time to change into the monoclinic.

The most convenient method of **preparing monoclinic sulfur** is to allow the liquid to cool very slowly to a temperature below its freezing point, but above 96°. This can be done by pouring the molten sulfur

[1] Two further modifications of sulfur have been shown to exist. S_π is found in liquid sulfur together with S_λ and S_μ, and is partly responsible for the changes in viscosity. Of all modifications it is the most soluble in carbon disulfide, even at very low temperatures, and is intensely yellow. S_ρ (orange yellow) is obtained in reactions in which sulfur is slowly deposited.

into an evaporating dish surrounded by boiling water. The liquid solidifies first at the upper surface, and is covered with a crust; if after the whole of the material has come to the temperature of the dish, the crust is broken, long needles of the monoclinic variety are found. The solid maintains this needle-like shape even when it is cooled to room temperature; but the needles which originally were glossy and quite translucent have become dull and opaque. When the material is examined with a magnifying glass, the needles are seen to consist, not of single long crystals as they were at the temperature of formation, but of masses of minute rhombic crystals cast into the shape of needles.

Amorphous Sulfur.—When liquid sulfur is very rapidly cooled by pouring it into cold water, an elastic, rubbery mass results. This material is partially soluble in carbon disulfide—the higher the temperature of the liquid immediately before pouring it into the water, the smaller the amount of the soluble component. Evidently the mass is a mixture of S_λ and of S_μ. The mixture gradually loses its elasticity and lustrous appearance, and becomes brittle and dull. At the same time its color changes. When first formed, the mass is dark brown. The higher the temperature of the liquid before cooling, the larger is the amount of S_μ and the darker the color of the chilled material. On standing, the mixture becomes paler, and after some time small rhombic crystals appear. Apparently the liquid was cooled past its freezing point so rapidly that crystals could not form. The result is amorphous sulfur, that is, supercooled liquid sulfur. The transformation of S_μ into S_λ also does not have time to reach completion, and the two liquids are therefore both present in the supercooled mass in varying amounts. The rigidity of the latter is explained as follows. As the temperature of liquids is lowered, their viscosity increases, and may ultimately become so large that they no longer flow freely. The supercooling of liquids to this extent is not an uncommon phenomenon. Ordinary glass is a supercooled liquid, with a viscosity so great at low temperatures that objects made of it permanently retain their shape. **Devitrification** of glass is slow crystallization of the supercooled liquid. Some chemists maintain that **only crystalline substances are solids;** all amorphous substances according to this point of view are supercooled liquids.

Sulfur Vapor.—Continued heating of liquid sulfur raises the temperature to the boiling point, 444.5°. Even gaseous sulfur is capable of undergoing changes, for at temperatures near the boiling point the density of the vapor indicates that the formula is S_8, while at very high temperatures the molecular weight seems to correspond to S_2. Evidence of the existence of molecules of intermediate molecular weight (e.g., S_6) is not lacking. The complete set of changes which sulfur undergoes when heated may be indicated by the following scheme:

$$S_{\text{rhombic}} \overset{96^\circ}{\rightleftharpoons} S_{\text{monoclinic}} \overset{119^\circ}{\rightleftharpoons} S_\lambda \overset{119\text{–}445^\circ}{\rightleftharpoons} S_\mu \overset{445^\circ}{\rightleftharpoons} S_8 \overset{445\text{–}1000^\circ}{\rightleftharpoons} S_2$$

The Chemical Properties of Sulfur.—Sulfur behaves in many respects like oxygen. It combines with all of the metals, except gold and platinum, to form sulfides; the sulfides of the two metals mentioned may be prepared by indirect means. In the reactions with most of the metals a considerable amount of heat is evolved. Sulfur reacts slowly with hydrogen; the hydrogen sulfide formed is not very stable. In these reactions sulfur acts by taking electrons from the atoms of the other elements just as does oxygen (see page 215.) But sulfur, unlike oxygen, also interacts very readily with elements which have a very decided tendency to take on electrons. Sulfur burns in air to form sulfur dioxide and traces of sulfur trioxide; it combines with fluorine to form sulfur hexafluoride, with chlorine to give sulfur monochloride and tetrachloride, and with many other electronegative elements. How two electronegative elements can react with each other will be taken up later.

Sulfur is used extensively in the industries. Most of it is converted into sulfuric acid; next in importance, is its employment in the vulcanizing of rubber and in the production of sulfite for paper manufacture. It is used in fungicides and insecticides, in the dye industry, and in the manufacture of matches. Mustard gas, well known as a war gas, is a sulfur compound.

Hydrogen Sulfide and the Sulfides

Preparation of Hydrogen Sulfide.—Hydrogen sulfide is prepared by the action of dilute solutions of strong acids on sulfides.

Hydrochloric acid and ferrous sulfide are most commonly employed:

$$FeS + 2HCl \rightleftharpoons H_2S\uparrow + FeCl_2 \qquad (1)$$

The reaction is one of ionic type; it proceeds forward because hydrogen sulfide is slightly ionized. The reaction is therefore one of displacement of a weak acid by a strong one (see pages 226 and 227). Action toward the right is favored also by the removal of the hydrogen sulfide from the solution as a gas, since it is not very soluble in water. The reaction will be discussed further in connection with the precipitation of sulfides.

Hydrogen sulfide is frequently formed as a product of reduction of sulfur compounds. It occurs in the decomposition of animal matter, such as in the rotting of eggs, and is found in some mineral waters, and in gases escaping from springs and volcanic openings. Its preparation from sulfides is so simple and cheap that other possible sources do not come into practical consideration.

Physical Properties of Hydrogen Sulfide.—The density of the gas and its composition indicate the formula H_2S. Its boiling point is about $-60°$ and its freezing point $-83°$, indicating moderately strong attractive forces between the molecules. It is slightly soluble in water; a saturated solution at 20° is approximately 0.1 molar.

Hydrogen sulfide is a poisonous substance. Breathing of air containing 1 part of the gas in 200 parts of air may lead to fatal results. Even in much greater dilution it causes severe headache and nausea. Experiments with it, or reactions in which it may be liberated, must be carried out in a hood.

Chemical Properties of Gaseous Hydrogen Sulfide.—Hydrogen sulfide is **not very stable**; it is noticeably dissociated into hydrogen and sulfur at 300°, and rise of temperature increases the dissociation according to the equation:

$$H_2S \rightleftarrows H_2 + S \qquad (2)$$

Both of the products of dissociation are readily combustible; and consequently hydrogen sulfide must catch fire when heated to the ignition temperature of hydrogen or sulfur because at that temperature it is dissociated to a very considerable extent. The

presence of free sulfur can be demonstrated in a flame of burning hydrogen sulfide by allowing the flame to play on a cold object. On this sulfur is deposited.

There are few other common reactions of hydrogen sulfide which may be ascribed to the dry gas. It reacts with sulfur dioxide:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \qquad (3)$$

Metals, exposed to an atmosphere containing hydrogen sulfide, become coated with a layer of sulfide and are thereby tarnished, but it is extremely doubtful whether this would occur with perfectly dry materials. Discussion of the reactions involved is taken up in the following paragraphs.

Behavior of Aqueous Solutions of Hydrogen Sulfide.—Hydrogen sulfide, in aqueous solution, is very slightly ionized. Practically all of the properties of the solution may be ascribed to the properties of the resulting ions and to the slight degree of ionization. The ionization, like that of all dibasic acids, proceeds in two steps:

$$H_2S \rightleftharpoons H^+ + HS^-, \quad (4) \quad \text{and,} \quad HS^- \rightleftharpoons H^+ + S^= \quad (5)$$

The combined reaction is:

$$H_2S \rightleftharpoons 2H^+ + S^= \qquad (6)$$

For most practical purposes the last equation may be used, since any action which removes hydrogen ion or sulfide ion must ultimately cause complete dissociation of the hydrogen sulfide into the simple ions.

Behavior of Hydrogen Sulfide as a Weak Acid.—Since hydrogen sulfide is so slightly ionized, it is a very weak acid and affects moist litmus but slightly. As an acid, it reacts with the more active metals to give hydrogen as illustrated by the reaction:

$$Fe + H_2S \rightarrow FeS + H_2 \qquad (7)$$

But because of the low concentration of hydrogen ion the reaction is very slow. The acid properties are shown further by the fact that it neutralizes bases. Since hydrogen sulfide is a dibasic

acid it forms two kinds of salts—**acid salts** by the neutralization of only one of the hydrogen ions, and **normal salts** by the neutralization of both of the hydrogen ions. These statements are illustrated by the equations:

$$H_2S + NaOH \rightleftharpoons NaHS + H_2O \quad (8)$$

$$NaHS + NaOH \rightleftharpoons Na_2S + H_2O \quad (9)$$

If two gram molecules of sodium hydroxide are added to one gram molecule of hydrogen sulfide in solution, sodium sulfide is obtained, although in the course of the reaction the acid sulfide is undoubtedly first formed. The equilibrium in these reactions is discussed below.

Hydrolysis of Sulfides.—Although hydrogen sulfide reacts with bases to form salts, the latter are hydrolyzed in aqueous solutions because they are salts of a weak acid. (See pages 230 and 235.) This is made clear by writing the reactions in ionic form:

$$Na^+ + HS^- + HOH \rightleftharpoons Na^+ + OH^- + H_2S \quad (10)$$

Both water and hydrogen sulfide are slightly ionized and a " pull " is exerted in both directions. Water, however, is far less ionized into H^+ and OH^- ion than is hydrogen sulfide into H^+ and HS^-, and the " pull " toward the left is much greater than that toward the right. Aqueous solutions of sodium hydrogen sulfide are therefore relatively slightly hydrolyzed. The situation in the case of solutions of sodium sulfide is quite different because the second hydrogen ion of hydrogen sulfide is much less readily dissociated than the first, as is true for all dibasic acids. In the reaction

$$2Na^+ + S^= + HOH \rightleftharpoons Na^+ + OH^- + Na^+ + HS^- \quad (11)$$

the " pulls " toward the right and toward the left are much more nearly equal than in the preceding action because the HS^- is dissociated into H^+ and $S^=$ ions somewhat less than water into H^+ and OH ions. In dilute solutions, therefore, in which there is a large excess of water, hydrolysis is almost complete, and the solutions are very basic in reaction.

The salts discussed are salts of the strong base, sodium hydroxide. Sulfides of weak bases are more extensively hydrolyzed than is sodium sulfide as may be seen from the equation for the hydrolysis of ammonium bisulfide:

$$NH_4^+ + HS^- + HOH \rightleftharpoons NH_4OH + H_2S \qquad (12)$$

Here the effects of the slight ionization of ammonium hydroxide and of hydrogen sulfide are added together in drawing the reaction to the right. Even in this case, the hydrolysis is not complete because the base is not nearly as weak as the acid. Normal ammonium sulfide, on the other hand, is completely hydrolyzed to the bisulfide. Sulfides of aluminium and chromium, the hydroxides of which are very weak bases, are also completely hydrolyzed.[1]

Double Decomposition of Hydrogen Sulfide with Salts, and the Interaction of Sulfides with Acids.—Since hydrogen sulfide is an ionogen, it interacts with salts by double decomposition. This type of reaction is best illustrated by taking up several cases. When hydrogen sulfide is passed through an aqueous solution of barium chloride no appreciable interaction occurs, because all of the substances involved, except hydrogen sulfide, are highly ionized:

$$Ba^{++} + 2Cl^- + H_2S \rightleftharpoons Ba^{++} + S^= + 2H^+ + 2Cl^- \qquad (13)$$

The removal of the hydrogen and sulfide ions to form slightly ionized hydrogen sulfide draws the reaction to the left; there is nothing to cause the reaction to go the other way. As the reaction proceeds in the direction indicated, the amount of hydrogen sulfide increases until the solution is finally saturated with it. Then the escape of the hydrogen sulfide as a gas causes the reaction to go to completion to the left.

On the other hand, the reaction:

$$Cu^{++} + SO_4^= + H_2S \rightleftharpoons CuS + 2H^+ + SO_4^= \qquad (14)$$

goes practically completely to the right because copper sulfide

[1] The hydrolysis of aluminium and chromium sulfides is favored also by the insolubility of the resulting hydroxides. (See page 535.)

(although a salt and highly ionized in solution) is so little soluble that its precipitation removes the sulfide ion more completely than does the formation of slightly ionized hydrogen sulfide. Manganous sulfide, MnS, is not very soluble in water; nevertheless the reaction:

$$Mn^{++} + 2Cl^- + H_2S \rightleftharpoons MnS + 2H^+ + 2Cl^- \qquad (15)$$

goes practically completely to the left. Evidently, in this instance, the removal of ions by the formation of the slightly soluble manganous sulfide is not complete enough to counteract the removal of the ions by the formation of slightly ionized hydrogen sulfide. Manganous sulfide must therefore be more soluble than copper sulfide, but less soluble than barium sulfide.

The **effect of the degree of ionization** of the acid is shown by the following illustration. Zinc sulfide is a fairly insoluble substance, but its solubility is sufficient to permit the following reaction to go chiefly to the left:

$$Zn^{++} + 2Cl^- + H_2S \rightleftharpoons ZnS\downarrow + 2H^+ + 2Cl^- \qquad (16)$$

But when zinc acetate, $Zn(C_2H_3O_2)_2$, is treated with hydrogen sulfide, complete precipitation of zinc sulfide occurs according to the equation:

$$Zn^{++} + 2C_2H_3O_2^- + H_2S \rightleftharpoons ZnS\downarrow + 2HC_2H_3O_2 \qquad (17)$$

The **combined** effect of the insolubility of zinc sulfide and of the weakness of acetic acid is sufficient to counterbalance completely the effect of the very slight ionization of hydrogen sulfide.

In the preceding discussion, action to the left represents action of an acid on a sulfide. If the sulfide is not very soluble in water, action to the left is accompanied by the disappearance of any of the solid sulfide suspended in the mixture; the sulfide therefore seems to dissolve. The **solubility of a sulfide in an acid** [1] is, consequently, determined by the **strength of the**

[1] It is self-evident that such a reaction is not only a process of solution. Nevertheless it is correct to say that the acid dissolves the sulfide in such cases, because the chemical interaction is preceded by solution of the sulfide, and because the direction of the chemical reaction is determined by the solubility.

acid and by the **solubility of the sulfide in water.** (See pages 252 to 253.) Copper sulfide, which (see equation 14) is very insoluble in water, is not dissolved even by strong acids like hydrochloric acid; less insoluble sulfides like zinc sulfide are completely soluble in an excess of a strong acid, because the excess of the acid introduces an excess of hydrogen ion and thus drives reaction (16) completely to the left. Sulfides of this class are not soluble in weak acids like acetic acid (equation 17), whereas manganous sulfide is soluble in acids as weak as acetic acid, but not in acids as weak as carbonic.

Precipitation of Sulfides and the Separation of Positive Ions.—Obviously some positive ions may be separated from others by the precipitation of sulfides. When hydrogen sulfide is passed through a solution of cupric and zinc chlorides, acidified with a little hydrochloric acid, it completely precipitates copper sulfide and leaves all the zinc ion in solution. Again, hydrogen sulfide completely precipitates zinc sulfide from a mixture of zinc and manganous acetates, and leaves all of the manganous ion in solution. But the process can be carried further. Reaction (15) can be driven completely to the right, instead of to the left, and manganous sulfide precipitated, by removing the hydrogen ion from the solution. This can be done by adding a base, the hydroxide ion of which unites with the hydrogen ion to form water. Ammonium hydroxide is generally used for the purpose. Since ammonium hydroxide and hydrogen sulfide react to form ammonium sulfide, the latter may be used instead of ammonium hydroxide and hydrogen sulfide, and the equation becomes:

$$Mn^{++} + 2Cl^- + 2NH_4^+ + S^= \rightleftharpoons MnS\downarrow + 2NH_4^+ + 2Cl^- \quad (18)$$

The reaction goes completely to the right because the only removal of ions is caused by the precipitation of manganous sulfide. But the addition of ammonium sulfide to barium chloride fails to precipitate barium sulfide (since the latter is soluble in water), and a method for separating barium and manganous ions is therefore available.

Relative Solubility of Various Sulfides.—Although the details of the separation of ions from each other by precipitation as sulfides are beyond the scope of this text, and must be sought for in books on qualitative analysis, a list of the sulfides arranged in the order of their relative solubilities is given. The solubility is indicated by stating the conditions under which the sulfides can be precipitated from salts of strong acids,

like the chlorides. As a matter of general interest the colors of the precipitated sulfides are placed in parentheses after the formula. In each group, the order is roughly that of increasing solubility.

TABLE XII

THE RELATIVE SOLUBILITIES OF THE SULFIDES OF THE MORE COMMON METALS

Sulfides Precipitable from Solutions Containing Concentrated Hydrochloric Acid.

As_2S_5, As_2S_3	(yellow)
HgS	(black)*
Ag_2S	(black)
CuS	(black)
Bi_2S_3	(dark brown)

Sulfides Precipitable in the Presence of Dilute Hydrochloric Acid, but not of Concentrated Hydrochloric Acid.

Sb_2S_3, Sb_2S_5	(orange red)†
SnS_2	(yellow)
CdS	(yellow)
PbS	(black)
SnS	(brown)

Sulfides not Precipitable from Solutions Containing even Dilute Hydrochloric Acid but Precipitable by Ammonium Sulfide.

ZnS	(white)
FeS, Fe_2S_3	(black)
NiS	(black)
CoS	(black)
MnS	(flesh colored)‡

Sulfides Soluble in Water, and therefore not Precipitated by Ammonium Sulfide.

MgS	Na_2S
CaS	K_2S
SrS	
BaS	

*A red modification of mercuric sulfide, known as cinnabar, is the form found in nature.

† Natural antimony sulfide is black.

‡ A green modification of manganous sulfide is precipitated under certain conditions which are, however, seldom encountered.

Specific Properties of the Sulfide Ion.—The reactions of hydrogen sulfide thus far discussed are reactions due (1) to the presence of hydrogen ion, or (2) to the slight degree of ionization of hydrogen sulfide, or (3) to the insolubility of its salts. The ability of sulfide ion to unite with hydrogen ion to form slightly ionized hydrogen sulfide and its ability to form insoluble salts with certain positive ions (as indicated in the list of the preceding paragraph) are **two of the properties of sulfide ion.**[1] Two other properties are of great importance in the behavior of sulfides and of hydrogen sulfide.

Sulfide ion has a great tendency to lose 2 electrons and revert to atomic sulfur. On this account **hydrogen sulfide and sulfides are excellent reducing agents** (see pages 217–220). Since oxidation and reduction are treated in detail in Chapter XVIII, it is sufficient at present to cite a number of illustrations of this property without discussing them fully. When solutions of hydrogen sulfide are exposed to air for a short time, sulfur is deposited as a result of the reaction:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S \qquad (19)$$

A similar reaction occurs when hydrogen sulfide is treated with iodine:

$$H_2S + I_2 \rightarrow 2HI + S \qquad (20)$$

Hydrogen sulfide reduces ferric chloride to ferrous chloride, according to the equation:

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + S + 2HCl \qquad (21)$$

To show that in these reactions the reducing agent, hydrogen sulfide, gives up electrons to the oxidizing agent, it is necessary merely to rewrite the last three equations, replacing all of the ionizable substances (without regard to their degree of ionization) by the ions they yield. Somewhat more complex are the reactions

[1] Attention is again called to the fact that sulfide ion, like most other negative ions, has very little tendency to unite with positive ions other than hydrogen ion, as is shown by the fact that practically all sulfides are highly ionized, even though they are slightly soluble. See page 240.

of hydrogen sulfide with potassium permanganate and potassium dichromate in acid solutions. The permanganate solution, originally purple, becomes colorless, showing that manganous ions, Mn^{++}, are formed; the orange dichromate solution becomes green as a result of the formation of chromic ions, Cr^{+++}. The reactions are discussed in detail in Chapter XVIII.

$$5H_2S + 2KMnO_4 + 3H_2SO_4 \rightarrow 5S + 2MnSO_4 + K_2SO_4 + 8H_2O \quad (22)$$

$$3H_2S + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3S + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O \quad (23)$$

Sulfide Ion Unites with Sulfur to form Polysulfide Ions.— Solutions of sodium sulfide or sodium hydrogen sulfide dissolve sulfur giving yellow to red solutions of sodium polysulfides. Ammonium sulfide and other soluble sulfides behave in the same way. Several different polysulfide ions seem to be capable of existence, for the sulfides can dissolve more than 1 gram atomic weight of sulfur per gram atomic weight of sulfide. There is evidence for the existence of compounds containing as many as 5 atoms of sulfur for each sulfide ion, and it is possible that even more sulfur can be combined in this way. In the case of sodium for instance, a series of polysulfides corresponding to the formula Na_2S_x, in which x may be 2, 3, 4, or 5, seems to exist. The larger the amount of sulfur in the polysulfide ion, the darker is the color of the solution. The mechanism of the formation of polysulfides is not understood. The reactions for their formation are represented as follows:

$$Na_2S + S \rightarrow Na_2S_2 \quad \text{or} \quad Na_2S + 4S \rightarrow Na_2S_5 \quad (24)$$

$$2NaHS + S \rightarrow Na_2S_2 + H_2S \quad (25)$$

When the polysulfides are treated with acids hydrogen sulfide is given off, and sulfur is precipitated. Nevertheless hydrogen polysulfides exist, but they are very unstable and, unless special precautions are taken, they decompose spontaneously giving the products just named. Polysulfides exist in nature—natural ferrous sulfide, iron pyrites, is a polysulfide, FeS_2.

EXERCISES

(1) Discuss from the point of view of Le Chatelier's rule the effect which increase of pressure must have on the equilibrium between rhombic and monoclinic sulfur. Take into consideration the relative densities of the two forms.

(2) Imagine a fairly large quantity of sulfur to be contained in a vessel. The sulfur completely surrounds the bulb of a thermometer. The vessel and its contents are gradually heated. By plotting temperatures as ordinates and the time as abscissae, show the temperature changes which must occur as the sulfur is slowly heated. Take into consideration the heat effects which accompany the transformation of rhombic to monoclinic and of liquid to gaseous sulfur.

(3) How is the formula of gaseous sulfur determined to be S_8 at lower, and S_2 at higher temperatures?

(4) Describe what occurs when liquid sulfur is heated. What evidence is there that the two substances, S_λ and S_μ exist?

(5) Why is the melting point of rapidly cooled liquid sulfur lower than that of the slowly cooled liquid?

(6) What is an amorphous substance supposed to be?

(7) Describe a reaction for the preparation of hydrogen sulfide, and explain why the reaction involved goes to completion.

(8) Which properties of an aqueous solution of hydrogen sulfide are due to the hydrogen ion?

(9) Explain why hydrogen sulfide acts **slowly** on active metals.

(10) (*a*) Give four properties of sulfide ion. (*b*) Write the equations for reactions illustrating each of these properties.

(11) Explain why normal sodium sulfide is more hydrolyzed than sodium acid sulfide.

(12) (*a*) Why is copper sulfide completely precipitated from an aqueous solution of cupric chloride ($CuCl_2$) by hydrogen sulfide? (*b*) Why is zinc sulfide incompletely precipitated by hydrogen sulfide from a solution of zinc chloride ($ZnCl_2$)? (*c*) How could the precipitation be made complete? (*d*) Why is manganous sulfide not precipitated at all from aqueous solutions of manganous chloride ($MnCl_2$) by hydrogen sulfide? (*e*) Why is manganous sulfide precipitated from such solutions by ammonium sulfide? (In answering all of these questions, first write the equations for the reactions involved, using the scheme employed in the text to show which are highly ionized, which slightly ionized, and which slightly soluble substances.)

(13) Note: the questions in this exercise are the reverse of those in Exercise 12.

(*a*) Why is cupric sulfide not dissolved by dilute hydrochloric acid?

(*b*) Why is zinc sulfide dissolved by dilute hydrochloric acid?

(*c*) Why is zinc sulfide not dissolved, and why is manganous sulfide dissolved by acetic acid?

(14) Explain why hydrogen sulfide and the sulfides are reducing agents. Illustrate your answer by an equation.

REFERENCES

The mining of sulfur is described concisely and diagrams of the apparatus used are given in

Martin and Foucar—Sulphuric Acid and Sulphur Products. Chapter I.

The invention and history of the American (Frasch) Process are described in addresses reprinted in the Journal of Industrial and Engineering Chemistry, Vol. **4**, 132–140 (1912). Chemical and Metallurgical Engineering, Vol. **24**, 65–72 (1921) contains an article by Bacon and Davis on Recent Developments in the American Sulphur Industry.

CHAPTER XVII

THE OXIDES AND OXYGEN ACIDS OF SULFUR

Other Compounds of Sulfur

When sulfides or polysulfides are strongly heated in air or in oxygen, sulfur dioxide, SO_2, is produced. This substance, a gas of characteristic pungent odor, may also be prepared by the action of copper on hot concentrated sulfuric acid:

$$Cu + 2H_2SO_4 \rightarrow SO_2 + CuSO_4 + 2H_2O \qquad (1)$$

Another method of preparation is the interaction of sulfites with strong acids:

$$Na_2SO_3 + 2HCl \rightarrow SO_2 + 2NaCl + H_2O \qquad (2)$$

Since oxygen is bivalent and generally electronegative, the sulfur in sulfur dioxide might be considered to be 4 positive. But the compound is not ionizable;[1] the union of oxygen and sulfur therefore probably differs in character from the union of oxygen and sodium in which 2 electrons are completely transferred from oxygen atom to sodium atoms, and in which sodium and oxygen ions are definitely formed. Although it is extremely useful to formulate the sulfur in the dioxide and related compounds as 4 positive, the student must bear in mind that this formulation does not imply that free sulfur ions with 4 positive charges exist, or that 4 electrons are completely transferred from the sulfur atom to the 2 oxygen atoms. In order to keep the distinction in mind, we shall say in this text that sulfur in these compounds has the **valence number,** 4+. In sulfur trioxide and in sulfuric acid, the valence number, 6+ will likewise be

[1] Liquid sulfur dioxide seems to be very slightly ionized. Probably the liquid substance contains a few molecules of the formula S_2O_4, which are the source of the ions.

assigned to sulfur. The same sort of problem will be encountered in connection with several other compounds, and a more detailed discussion is, on that account, deferred to the chapter on the structure of atoms. (See page 367.)

Properties of Sulfur Dioxide and of Sulfurous Acid.—At room temperatures sulfur dioxide is a gas. It condenses to a colorless liquid at $-10°$, and freezes at $-73°$; the liquid at 50° has a vapor pressure of only 8 atmospheres. Its molecules evidently exert considerable attraction on each other, and the gas is readily liquefied by pressure even at room temperature. In this condition it may be purchased in small steel tanks. Owing to the large attractive forces between the molecules, the gas absorbs a considerable amount of heat when it expands suddenly from a highly compressed condition, and this property leads to its use in the smaller types of refrigerating machines. Sulfur dioxide is quite soluble in water; a saturated aqueous solution is approximately 3 molar at 0°, and 1.5 molar at 20°.

The gas is not very reactive when dry. The more active metals when heated in it are converted into oxides and sulfides; its interaction with hydrogen sulfide has already been mentioned (page 250). But most of its reactions occur in aqueous solution. When it is dissolved in water, a part of the dissolved gas reacts with water to form **sulfurous acid**:[1]

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \qquad (3)$$

Sulfurous acid is a moderately weak acid, dissociating in two steps:

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^- \qquad (4a)$$

and

$$HSO_3^- \rightleftarrows H^+ + SO_3^= \qquad (4b)$$

As always in such cases, the first hydrogen ion is dissociated from the acid more readily than the second. As a dibasic acid, sulfurous acid gives two series of salts, the acid and the normal **sulfites.** The normal sulfites are somewhat hydrolyzed to the

[1] Sulfur dioxide combines with water to form hydrates. This reaction is probably an intermediate step in the formation of sulfurous acid.

acid sulfites and the corresponding base, and therefore give an alkaline reaction in aqueous solution if the base is strong; the acid sulfites are somewhat less hydrolyzed to sulfurous acid and the base (see Table XI, page 234). The slight ionization of sulfurous acid also allows it to be displaced from its salts by stronger acids, as illustrated in the preparation of sulfur dioxide from sulfites (equation 2). In this reaction the sulfurous acid is first liberated in solution; it then decomposes into sulfur dioxide and water. Most of the salts of sulfurous acid, i.e., the sulfites, except those of the alkali metals, are slightly soluble in water, but the acid sulfites are soluble. All simple sulfites are dissolved by strong acids because of the slight degree of ionization of sulfurous acid.

Sulfur dioxide, sulfurous acid, and the sulfites are used as **bleaching** agents. The bleaching properties of these substances are due to their complex reactions with the organic dyes, which cannot be discussed here. The sulfites are extensively used in the manufacture of paper; their function is to separate the fibers of cellulose in wood pulp.

Sulfur dioxide and the compounds related to it are **reducing agents.** They react slowly with the oxygen of the air, decolorize potassium permanganate in acid solution, and reduce chromates. The equations for these reactions are as follows:

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4 \qquad (5)$$

$$5Na_2SO_3 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5Na_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O \qquad (6)$$

$$3Na_2SO_3 + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3Na_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O \qquad (7)$$

The halogens also oxidize sulfurous acid; when iodine is used the reaction is reversible unless the concentration of the sulfuric acid is kept quite low:

$$H_2SO_3 + I_2 + H_2O \rightleftarrows H_2SO_4 + 2HI \qquad (8)$$

Sulfurous acid may act also as an **oxidizing agent,** as illustrated by its reaction with hydrogen sulfide (page 250). The behavior of sulfur dioxide and the related compounds as oxidizing and reducing agents will receive further discussion in the next chapter.

The oxidizing and reducing properties of these compounds might raise the question whether it is not possible for them to oxidize and reduce themselves. As a matter of fact this is what occurs when **sulfites are heated.** Thus solid sodium sulfite gives sodium sulfate and sodium sulfide. Sodium sulfate is an oxidation product of sulfites, and sodium sulfide is a reduction product:

$$4Na_2SO_3 \rightarrow 3Na_2SO_4 + Na_2S \qquad (9)$$

Acid sulfites behave in entirely analogous fashion except that heating first converts them into the normal sulfites:

$$2NaHSO_3 \rightarrow Na_2SO_3 + SO_2 + H_2O \qquad (10)$$

The corresponding reactions do not occur in aqueous solution, probably because a condition of equilibrium is reached which, in the presence of the acid formed, lies on the side of the sulfite.

Finally the property of normal sulfites in aqueous solutions to combine when heated with free sulfur forming **thiosulfates** may be mentioned:

$$Na_2SO_3 + S \rightarrow \underset{\text{Sodium Thiosulfate}}{2Na_2S_2O_3} \qquad (11)$$

The thiosulfates thus formed are quite stable, but on addition of an acid they decompose completely into sulfur dioxide, sulfur, and water. This reaction indicates that free thiosulfuric acid is very unstable. The most commonly used reaction of thiosulfates is that with iodine, which occurs readily in solution. As the iodine is used up, its color becomes less and less intense, and the completion of the reaction is indicated by the disappearance of the color. This makes it possible to determine how much iodine was originally present, by measuring the amount of thiosulfate solution required to discharge the color. The equation is

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \qquad (12)$$

The substance, $Na_2S_4O_6$, is called **sodium tetrathionate.** It is one of many complex sulfur compounds.

The reaction of sulfur with sulfites is interesting from a theoretical point of view also. It recalls two other reactions. In the first place it is like the reaction of sulfites with oxygen, which may be written as follows to bring out the analogy to equation (11):

$$Na_2SO_3 + O \rightarrow Na_2SOO_3.$$

On the other hand, the ability of sulfites to dissolve sulfur suggests the similar property possessed by sulfides. According to the first analogy sodium thiosulfate might be considered to be built up according to the formula $NaOSONa$; the second analogy leads to the formula $NaOSSNa$. Thiosulfates possess properties in accord with both of these formulae. It is not yet decided which formula is correct.

Sulfur Trioxide.—When sulfur is burned a small amount of sulfur trioxide, SO_3, is obtained, in addition to sulfur dioxide, the chief product of reaction. Evidently sulfur dioxide can react with oxygen:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 \qquad (13)$$

Under ordinary conditions, the formation of sulfur trioxide in this way is an extraordinarily slow process. The velocity of all reactions is increased by rise of temperature, but in this case raising the temperature is not a feasible method of making the desired reaction proceed at appreciable speed. The reaction is reversible; at temperatures above 500° the trioxide is decomposed to a considerable extent, and at 1000° the decomposition is complete. In order to make sulfur trioxide by oxidation of sulfur dioxide, a catalytic agent must therefore be employed. Finely divided platinum deposited on asbestos is most commonly employed. Other catalysts, such as ferric or vanadium oxides, have been used, but they are not as effective as platinum. The reaction is carried out at about 400°, a temperature at which decomposition of sulfur trioxide is inappreciable.

This method for the manufacture of sulfur trioxide, known as the "**contact process,**" is of very great industrial importance because the sulfur trioxide thus prepared can be dissolved in water to make **sulfuric acid.** It is therefore interesting to know that the catalytic effect of platinum was discovered early in the nineteenth century by Davy, and that the application of the reaction to the manufacture of sulfuric acid was patented by Phillips in 1831. Nevertheless the manufacture of the acid in this way did not become a practical process until about 1901

because of the many difficulties encountered in large scale operations. Only two of these need be discussed here. In the first place the platinum used as catalyser quite rapidly loses its effectiveness; it is of course too expensive to permit of frequent renewals. Not until it was discovered that impurities in the sulfur dioxide caused the loss of efficiency of the catalyst could the process be made successful. It has since been found that catalysts of many sorts are affected by small amounts of substances which rob them of their catalytic properties—such substances are frequently called catalyst poisons. By removing the poisons—unburned sulfur, traces of mercury, phosphorus and arsenic compounds—the contact process was made successful. A second difficulty encountered was that the sulfur trioxide, obtained in the process as a fume suspended in the excess of gas, passes as a sort of fog or mist through the water, used as an absorbent. This difficulty was overcome by dissolving the sulfur trioxide in fairly concentrated sulfuric acid. The trioxide reacts with the water in the solution according to the equation:

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (14)$$

By continually adding water and passing sulfur trioxide into the original sulfuric acid, a small amount of the latter is converted into as large a quantity as may be desired. Cast-iron vessels, which are not attacked by concentrated sulfuric acid, are employed.

Sulfur trioxide, when first prepared, is a colorless liquid which boils at 45° and solidifies at about 18°. It is soluble in phosphorus oxychloride ($POCl_3$), and in this solvent its molecular weight is 80, as shown by the lowering of the freezing point of the solvent. But if the liquid sulfur trioxide is allowed to stand, it gradually solidifies to an asbestos-like solid which melts at 25° and, like the liquid, volatilizes quite easily. The solid form also is soluble in phosphorus oxychloride but its molecular weight in this solvent is 160, indicating the formula S_2O_6.[1] Evidently the reaction is:

$$2SO_3 \rightleftarrows S_2O_6 \qquad (15)$$

[1] The correctness of the data on freezing points and molecular weights of the two forms of sulfur trioxide has, however, been questioned. See Lichty, Journal of the American Chemical Society, Vol. **34,** p. 1440 (1912).

The chemical properties of the trioxide, as both forms are called, are very much like those of concentrated sulfuric acid. Its most important reaction is its union with sulfuric acid to form **pyrosulfuric acid** ($H_2S_2O_7$). The trioxide is also obtained by heating ferric sulfate to high temperatures, by heating pyrosulfates such as sodium pyrosulfate, $Na_2S_2O_7$, or by distilling sulfuric acid in the presence of phosphorus pentoxide, which reacts according to the equation:

$$H_2SO_4 + P_2O_5 \rightarrow SO_3 + 2HPO_3 \qquad (16)$$

The Manufacture of Sulfuric Acid.—Although more and more of the sulfuric acid used in science and the industries is being made by the contact process, an older method of manufacture is still extensively employed. Owing to the fact that all impurities must be removed from the reacting materials in the contact process, this method of manufacture yields a very pure product. It is therefore now used almost exclusively for the preparation of the better grades of the acid. Its use is advisable also when acid of high concentration is desired, since as has been pointed out, the sulfur trioxide is most efficiently absorbed by concentrated sulfuric acid. In the contact process, sulfur trioxide is actually an intermediate product, and fuming sulfuric acid—sulfuric acid which contains an excess of sulfur trioxide—can thus readily be prepared.

The older process for the manufacture of sulfuric acid, known as the **lead chamber process,** does not involve the isolation of sulfur trioxide, but consists essentially of the reaction

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad (17)$$

This reaction likewise does not proceed with appreciable velocity at ordinary temperatures, and here also rise of temperature cannot be used to hasten the action because the product decomposes at elevated temperatures. Hence a catalytic agent must again be used. The catalytic agent in this case is nitrogen dioxide, NO_2.[1] Although the chamber process is one of the oldest of

[1] Since the nitrogen dioxide unquestionably takes part in the reaction, it is perhaps not quite exact to call it a catalytic agent in this reaction. But until the nature of catalysis is better understood, no great error is made by a rather broad use of the term.

large scale chemical operations, the reactions which occur are not yet thoroughly understood. It is supposed that the nitrogen dioxide unites with sulfur dioxide, water and oxygen to form an intermediate compound, which subsequently decomposes into sulfuric acid and regenerates the nitrogen dioxide. A number of such compounds have been suggested by various workers in the field, but there is as yet no unanimity of opinion on the subject. The apparatus used in the chamber process is quite complex and need not be described. It may be mentioned, however, that the first interaction of sulfur dioxide, water and oxygen takes place in enormous lead chambers from which the process takes its name.

The Physical Properties of Sulfuric Acid.—Sulfuric acid, containing no excess of water or of sulfur trioxide, boils at about 270°. Some sulfur trioxide passes off as a vapor, and the remaining solution therefore contains an excess of water. But when the concentration of the sulfuric acid in the solution has fallen to 98.3 per cent, the boiling point becomes constant, at 338°, and the sulfuric acid solution distills over unchanged.[1] Conversely, dilute solutions of sulfuric acid when boiled lose water until a mixture of the same composition and boiling point is obtained. The freezing point of the 100 per cent acid is about −10°, but it is greatly affected by the addition of either water or of sulfur trioxide. The freezing point changes indicate the existence of 2 hydrates, $H_2SO_4 \cdot H_2O$ and $H_2SO_4 \cdot 4H_2O$, and of the compound $H_2SO_4 \cdot SO_3$, more commonly written $H_2S_2O_7$ and called pyrosulfuric acid.[2] The hydrates, especially the monohydrate, are fairly stable compounds; as a result, sulfuric acid containing only a little water has a very low aqueous tension at ordinary temperature. The large amount of heat liberated

[1] A great many different values are given by various writers for the boiling points of sulfuric acid and the constant boiling mixture of acid and water. The data in the text refer to a pressure of approximately 755 mm. For the normal boiling points of the pure acid and the constant boiling mixture, 330° and 338°, respectively, are often given but there is no unanimity among different writers on this point.

[2] The liquid obtained by dissolving sulfur trioxide in concentrated sulfuric acid is called Nordhausen or fuming sulfuric acid. The fuming is due to the escape of the trioxide from the solution.

when concentrated sulfuric acid is diluted with water may also be related to the tendency of the acid to react with water.

The Chemical Properties of Sulfuric Acid.—Concentrated sulfuric acid is a powerful oxidizing agent as is shown in numerous reactions. This property has already been encountered in its reaction with bromides and iodides (pages 151 and 160) and with copper (page 166). These reactions and other illustrations of this property will be discussed in the next chapter. Sulfuric acid is a moderately strong acid. In concentrated solutions it ionizes chiefly to give bisulfate (HSO_4^-) and hydrogen ion, whereas in dilute solutions dissociation into sulfate ions ($SO_4^=$) and hydrogen ions is practically complete. It is, in other words, a dibasic acid and, therefore, forms both normal and acid salts. If the base used is highly ionized, the normal salts are not appreciably hydrolyzed. The acid sulfates give a decidedly acid reaction in solution, because the HSO_4^- dissociates quite largely into H^+ and $SO_4^=$ after the first H^+ has been removed. Most of the sulfates are soluble in water. The common exceptions are barium, strontium and lead sulfates, which are very insoluble, and calcium sulfate, which is only slightly soluble. All of these sulfates are soluble in concentrated sulfuric acid, which converts them into bisulfates, but they are not soluble in acids like hydrochloric acid.

The **differences in the behavior of dilute** and of **concentrated sulfuric acid** are in most instances such as might be predicted. The dilute solutions have a much lower boiling point since they contain more water. Consequently mixtures containing the dilute solutions cannot be heated as high as can mixtures containing the concentrated acid. For this reason, many reactions for which elevated temperatures are required cannot be carried out with the dilute acid. Reactions in which the low aqueous tension of concentrated sulfuric acid is of importance do not take place in dilute solutions, because these have an aqueous tension approaching that of water. The fact that dilute solutions ionize chiefly into $SO_4^=$ whereas concentrated solutions yield chiefly HSO_4^- is not surprising, since the first hydrogen ion of any polybasic acid is formed most readily, and dilution favors ionization. The only unexpected difference is in the oxidizing

properties. Dilute sulfuric acid acts so slowly in oxidation and reduction reactions that it is usually considered to be without oxidizing power. Although this is not correct, the slowness of its oxidizing action does make the dilute acid **practically** useless as an oxidizing agent.

The Reasons for the Importance of Sulfuric Acid in Chemistry.—A little consideration of the properties of sulfuric acid will make clear why the substance plays such an important rôle in chemistry. In its manufacture, only sulfur dioxide and air are used in large quantities; the catalytic agents are used over and over again with but small losses. Since sulfur dioxide is made from sulfur or from sulfides (both of which are cheap) the acid is relatively inexpensive. It has a high boiling point, and is therefore used in liberating more volatile acids such as hydrofluoric, hydrochloric and nitric acids from their salts (pages 159 and 314). It is a strong acid, and is therefore employed to liberate weaker acids from their salts, or to dissolve salts of weak acids (pages 226, 238, 249, 252). As a strong acid it liberates hydrogen when brought into contact with the more active metals. It reacts with metallic oxides, and is used to clean the surfaces of metals. It is a strong oxidizing agent in concentrated solutions, and therefore attacks all but the most inactive metals and enters into a multitude of other reactions of oxidation and reduction. Its concentrated solution has a very low aqueous tension, and on this account is an excellent and convenient drying agent. It is used to remove water from moist materials placed near it in closed vessels called desiccators, or from gases bubbled through it.

In reactions with organic compounds at elevated temperatures, sulfuric usually acts simultaneously as a dehydrating and oxidizing agent. Thus many organic substances are charred and partially oxidized with the simultaneous removal of water.

Other Compounds of Sulfur.—In the foregoing, only those compounds of sulfur which the beginner in chemistry is likely to encounter have been discussed. Sulfur is a constituent of a large number of organic compounds, such as certain dyes and drugs and proteins, which cannot be taken up in this text although they are of great importance to industry and in living organisms. Of the remaining inorganic com-

pounds only a few will be mentioned. Hyposulfurous acid ($H_2S_2O_4$) and especially its salts are of considerable industrial importance, because they are powerful reducing agents. A series of acids, the polythionic acids, the formulae of which may be represented by $H_2S_nO_6$ (in which n is 2, 3, 4, 5, or 6) are interesting in connection with the general question of the structure of inorganic compounds.[1] Per-monosulfuric acid (H_2SO_5) and per-disulfuric acid [2] ($H_2S_2O_8$) are powerful oxidizing agents. The salts of the latter are used industrially. Both acids are obtained at the anode when cold concentrated solutions of sulfuric acid are electrolyzed. The reactions may be represented as follows:

$$2HSO_4^- \rightarrow H_2S_2O_8 + 2\epsilon \qquad (18)$$

Per-disulfuric acid reacts with water to give per-monosulfuric acid and sulfuric acid:

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \qquad (19)$$

Per-monosulfuric acid reacts further with water to give hydrogen peroxide and sulfuric acid:

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \qquad (20)$$

A method for the manufacture of hydrogen peroxide is based on these reactions.

The halides of sulfur have already been mentioned (page 155). The monochloride is used in the manufacture of rubber products. In addition to the simple halogen compounds, sulfuryl chloride, SO_2Cl_2, monochlorsulfonic acid, $HOSO_2Cl$, thionyl chloride, $SOCl_2$, and similar fluorine compounds exist. They are of considerable theoretical and some practical importance. All except sulfur hexafluoride are readily decomposed by water. Sulfuryl chloride when it reacts with water yields sulfuric acid and hydrogen chloride:

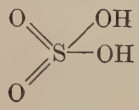
$$SO_2Cl_2 + 2HOH \rightarrow SO_2(OH)_2 + 2HCl \qquad (21)$$

This fact is used as an argument in favor of the idea that the atoms

[1] Structure of compounds is discussed in the chapter on the Structure of Atoms, and in the chapter on Carbon Compounds.

[2] Per-monosulfuric acid is sometimes called Caro's acid, and per-disulfuric acid is usually called per-sulfuric acid.

composing sulfuric acid molecules are joined to each other as is indicated in the following formula:



Such a formula is called a structural formula (see pages 418–428 for other illustrations). It shows that sulfuric acid, like all other oxygen acids, might be looked upon as an hydroxide. This idea will be useful in some of the discussions encountered later. Substances related to oxygen acids as is sulfuryl chloride are called **acid chlorides.** Thus, thionyl chloride is the acid chloride of sulfurous acid, and sulfuryl chloride the acid chloride of sulfuric acid.

Finally, the compounds of sulfur and nitrogen alone and of sulfur, nitrogen and other elements might be mentioned. They constitute an important class of substances which, although they are of great interest and importance, are too complex to be taken up here. Other sulfur compounds will be mentioned in connection with some of the other elements.

EXERCISES

(1) (*a*) Give several methods for the preparation of sulfur dioxide. (*b*) If the reagents needed for each of them were procurable with equal ease and at the same cost, which method should you consider the most convenient, and why?

(2) (*a*) What are the reasons for believing that the molecules of sulfur dioxide attract each other with considerable force? (*b*) Why is sulfur dioxide used in refrigerating machines?

(3) What experiments would you perform to prove that sulfurous acid is a moderately weak acid?

(4) (*a*) What is obtained when an aqueous solution of sodium hydroxide is saturated with sulfur dioxide? (*b*) How would you convert the product obtained in (*a*) into normal sodium sulfite?

(5) Explain why sulfur dioxide is liberated when a sulfite is treated with a strong acid.

(6) Upon what data must the conclusion that gaseous sulfur dioxide has the formula SO_2 rather than S_2O_4 be based?

(7) (*a*) Describe the contact process for the manufacture of sulfuric acid. (*b*) When is this process particularly satisfactory?

(8) In what way does the meaning of the term catalyst as used in the text in connection with the chamber process, differ from the usage in connection with the contact process?

(9) (*a*) List the important physical and chemical properties and the uses of sulfuric acid. (*b*) Explain why sulfuric acid is adapted to each of the uses mentioned in the text.

(10) When two open vessels, one containing crystals of $Na_2SO_4 \cdot 10H_2O$ and the other concentrated sulfuric acid are placed into the same closed vessel, the hydrate loses its water. Explain.

REFERENCES

Chase and Pierce—Journal of Industrial and Engineering Chemistry, Vol. 14, 498, (1922) describe a modern installation of the "contact process."

Martin and Foucar—Sulphuric Acid and Sulphur Products. Chapter II, describes, in very concise form and with many diagrams of apparatus, the manufacture of sulfuric acid by both processes.

Rogers—Manual of Industrial Chemistry (1921). Chapter IV is a detailed, fully illustrated and well written account of the manufacture of sulfuric acid.

CHAPTER XVIII

REACTIONS OF OXIDATION AND REDUCTION

EQUATIONS representing the union of elements, the dissociation of compounds, or double decompositions, can always be easily written when the formulae of all of the substances involved are known. Equations for certain reactions in which oxidation and reduction occur, cause more difficulty, and a number of schemes have been devised to simplify the problem. The difficulties are very readily overcome by making use of the hypothesis (see pages 217–220), that the oxidizing agent gains electrons and the reducing agent gives them up.

Balancing of Simple Equations of Oxidation and Reduction.— The application of this hypothesis to the problem of balancing equations may be explained very simply by making use of the reactions of hydrogen sulfide with ferric chloride and with iodine (page 256). In both reactions sulfide ion goes over to atomic sulfur by giving up 2 electrons. In the former the ferric ion, which is the oxidizing agent, takes up 1 electron, thus becoming ferrous ion. These facts may be represented by the following (incomplete) equation, in which an arrow pointing downward ($\downarrow$) indicates the element which gives up electrons, an arrow pointing upward ($\uparrow$) the element which takes up the electrons, and the number preceding the symbol, ϵ, the number of electrons lost or gained:

$$\overset{\overset{2-}{\downarrow}}{\underset{2\epsilon}{H_2S}} + \overset{\overset{3+}{\uparrow}}{\underset{1\epsilon}{FeCl_3}} \rightarrow \overset{0}{S} + \overset{2+}{FeCl_2}\,[1] \qquad (1a)$$

[1] The valences or valence numbers are indicated above the symbols of atoms, the valence of which undergoes change. The valence of the free element is considered to be 0.

The equation is not balanced; neither is the number of electrons lost by the reducing agent equal to the number taken up by the oxidizing agent. In order to make these numbers equal, 2 molecules of ferric chloride must be used for 1 of hydrogen sulfide. From these amounts of the reacting substances 1 atom of sulfur [1] and 2 molecules of ferrous chlorides are obtained. Likewise, in order to equalize the numbers of hydrogen and chloride ions on the two sides of the equation, 2 molecules of HCl must be added to the right side. The equation becomes:

$$\overset{2-}{H_2S} + 2\overset{3+}{FeCl_3} \rightarrow \overset{0}{S} + 2\overset{2+}{FeCl_2} + 2HCl \qquad (1b)$$

$$\downarrow \quad \uparrow$$

$$2\epsilon = 2 \times 1\epsilon$$

In the reaction between hydrogen sulfide and iodine, the latter is the oxidizing agent. Each atom of iodine takes up 1 electron to become iodide ion:

$$\overset{2-}{H_2S} + \overset{0}{I_2} \rightarrow \overset{0}{S} + 2\overset{1-}{HI} \qquad (2)$$

$$\downarrow \quad \uparrow$$

$$2\epsilon = 2 \times 1\epsilon$$

Obviously, the equation is balanced; this is because the number of electrons lost and taken up is equal for the proportions of reagents originally written down. The fundamental step in balancing equations for oxidation and reduction reactions is thus very simple. It is only necessary to choose the numbers of molecules of oxidizing agent and of reducing agent so that the **number of electrons taken up is equal to the number lost.**[2] Before this can be done it is of course necessary to determine (by inspection of all of the molecules or ions involved in the reaction) which substances lose electrons, which take them up, and what are the numbers of electrons involved.

A few other examples of the method of balancing equations

[1] Solid sulfur unquestionably does not consist of sulfur atoms (page 246), but it is unnecessary to take this fact into consideration. If the formula S_8 were used it would merely be necessary to multiply the final equation by 8.

[2] The successful balancing of such equations is indicated in the text by the equals sign (=) between the number of electrons lost and gained.

of this type, chosen from the reactions mentioned in the preceding chapter, may now be discussed in more detail. When sulfurous acid reacts with chlorine, sulfuric and hydrochloric acids are formed:

$$H_2SO_3 + Cl_2 \rightarrow H_2SO_4 + 2HCl \qquad (3a)$$

Each of the 2 chlorine atoms in the chlorine molecule takes up 1 electron to become chloride ion (Cl^-). To determine the change which occurs in the reducing agent, H_2SO_3, the valence number of each of its constituent elements, before and after the reaction, must be examined. In all such cases the procedure is greatly simplified by remembering that, except in reactions which liberate oxygen or hydrogen, **the valence of hydrogen and of oxygen does not change.**[1] In the reaction under discussion, attention may therefore be centered on the sulfur. It has been pointed out that in sulfur dioxide, sulfurous acid, and sulfites the valence number 4+ may be assigned to sulfur, and that in sulfur trioxide, sulfuric acid, and sulfates the sulfur may be given the valence number 6+. In going from sulfurous to sulfuric acid, the sulfur may be considered to **give up** 2 electrons.[2] These conclusions are summarized in the equation:

$$\overset{4+}{H_2SO_3} + \overset{0}{Cl_2} \rightarrow \overset{6+}{H_2SO_4} + 2\overset{1-}{HCl} \qquad (3b)$$

$$\downarrow 2\epsilon \quad = \quad \uparrow 2\epsilon$$

Since the number of electrons lost is equal to the number taken up, the equation is balanced so far as oxidation and reduction is concerned. But there are 4 hydrogens and 4 oxygens on the right side of the equation, while there are only 2 hydrogens and 3 oxygens on the left. The deficiency on the left is evidently

[1] The formation of peroxides, in which the negative ion is $O_2^=$, of peracids (see page 270) and of certain organic compounds are exceptions to this statement. These substances are so seldom encountered that in general they need not be considered in balancing equations.

[2] The charge on an ion is due to the difference between the positive charge on the nucleus of the atom and the negative charge of the electrons in the outer shell of the atom (pages 192–194). In order to become more positive an ion must lose additional electrons.

exactly 1 molecule of water. Since the reaction takes place in aqueous solution, water is available, and the final equation is:

$$\overset{4+}{H_2SO_3} + \overset{0}{Cl_2} + H_2O \rightarrow \overset{6+}{H_2SO_4} + 2\overset{1-}{HCl} \qquad (3c)$$

$$\downarrow 2\epsilon \quad = \quad \uparrow 2\epsilon$$

For further practice, take the reaction between concentrated sulfuric acid and hydriodic acid in which the products obtained are shown in the following unbalanced equation:

$$H_2SO_4 + HI \rightarrow H_2S + I_2 \qquad (4a)$$

Here iodide ions give up 1 electron each to become uncharged molecular iodine. Sulfur changes from 6+ in sulfuric acid to 2− in hydrogen sulfide, and to do this must take up 8 electrons. These statements are indicated as follows:

$$\overset{6+}{H_2SO_4} + \overset{1-}{HI} \rightarrow \overset{2-}{H_2S} + \overset{0}{I_2} \qquad (4b)$$

$$\uparrow 8\epsilon \qquad \downarrow 1\epsilon$$

The equation is not balanced because the number of electrons lost is not equal to that taken up. Eight times as many electrons are required as are furnished by 1 molecule of hydrogen iodide, and 8 molecules of the latter must therefore be used. Since all of the iodide ions go over to iodine molecules, 4 of the latter are obtained:

$$\overset{6+}{H_2SO_4} + 8\overset{1-}{HI} \rightarrow \overset{2-}{H_2S} + 4\overset{0}{I_2} \qquad (4c)$$

$$\uparrow 8\epsilon \quad = \quad \downarrow 8\times 1\epsilon$$

Although the equation is balanced from the point of view of the oxidizing and reducing agents, there are 4 oxygens and 10 hydrogens on the left and no oxygens and only 2 hydrogens on the right. But again the deficiency can be expressed exactly in terms of molecules of water, and the final equation is:

$$\overset{6+}{H_2SO_4} + 8\overset{1-}{HI} \rightarrow \overset{2-}{H_2S} + 4\overset{0}{I_2} + 4H_2O \qquad (4d)$$

$$\uparrow 8\epsilon \quad = \quad \downarrow 8\times 1\epsilon$$

It is invariably found, as in equations (3) and (4), that hydrogen and oxygen can be balanced at sight by introducing the correct number of water molecules into the equation **after** the fundamental balance of the oxidizing and reducing agents has been made by the method described. When the student becomes more familiar with the method, he will find it unnecessary to work out the equations in steps as in these first illustrations; the simplified procedure, to be used when all the steps are clearly understood, will be shown below.

Methods of Determining the Valence Number of Atoms in Compounds.—It is evident from the steps in balancing equations involving sulfuric or sulfurous acid, that it is important to assign the correct valence number to every atom represented in the equation. No difficulty is encountered in doing this when all of the substances are salts or acids which yield simple ions of known valence. For substances containing compound ions like sulfate, sulfite, nitrate, permanganate, and so on, the valence numbers cannot always be determined at sight, but there are several very simple methods for doing so. The valence number 4+ was chosen for sulfur in sulfurous acid because the latter is formed from sulfur dioxide by the addition of water. In sulfur dioxide the sulfur obviously must be considered to be 4+ if the oxygen is 2−. In the same way the valence number 6+ was chosen for sulfur in sulfuric acid because the latter is derived from sulfur trioxide. This method can be generalized quite easily so as to be applicable to all compound ions.

The following method, however, is simpler than that described in the preceding paragraph. Sulfate ion is 2−, as shown by the formula of sulfuric acid, H_2SO_4, which ionizes into 2 hydrogen ions and 1 sulfate ion. If each of the oxygens is 2−, the total negative charge due to oxygen is 8−. The ion, as a whole, is only 2−, hence, the eight negative charges on the oxygens may be looked upon as being counterbalanced by six positive charges on the sulfur. In analogous fashion the valence number of the chromium in dichromate ion may be determined. The dichromate ion is 2−, as shown by the formula of dichromates (for example $K_2Cr_2O_7$). The 7 oxygens are considered to be 2− each, making a total of 14 negative charges, and these must

be counterbalanced by 12 positive charges on the 2 chromiums in the compound ion. To each chromium atom the valence number 6 + is therefore assigned. For further practice in determining the valence number of atoms in compound ions, the student is referred to problem (5), page 288.

Balancing of more Complicated Oxidation and Reduction Equations.—Chromates, permanganates, and many other oxidizing agents are usually used in acid solutions. In most instances the acid takes part in the reaction, and this fact must of course be shown in the equation.[1] The principle used in balancing the simpler equations can also be used for the more complex ones, as shown in the case of the reaction between hydrogen sulfide and potassium permanganate in the presence of sulfuric acid. In order to make the matter perfectly clear, each step in balancing the equation will be discussed by itself. Application of the scheme described in the preceding paragraph shows that the manganese in permanganate ion has the valence number 7+; the disappearance of the purple color is experimental proof that manganous ions (Mn^{++}) are formed during the course of the reaction (see page 257). The manganese atom in the permanganate ion may therefore be said to take up 5 electrons. On the other hand the sulfide ion, which is the reducing agent, goes over to free sulfur, and therefore gives up 2 electrons. These statements are summarized in the incomplete equation:

$$\overset{\overset{7+}{\uparrow}}{\underset{5\epsilon}{KMnO_4}} + \overset{\overset{2-}{\downarrow}}{\underset{2\epsilon}{H_2S}} + H_2SO_4 \rightarrow \overset{2+}{Mn} + \overset{0}{S} \qquad (5a)$$

In order to balance the oxidizing and reducing agents, 2 molecules of permanganate must react with 5 of hydrogen sulfide. Two manganous ions and 5 sulfur atoms are formed:

$$\overset{\overset{7+}{\uparrow}}{\underset{2\times5\epsilon}{2KMnO_4}} + \overset{\overset{2-}{\downarrow}}{\underset{5\times2\epsilon}{5H_2S}} + H_2SO_4 \rightarrow 2\overset{2+}{Mn} + 5\overset{0}{S} \qquad (5b)$$

[1] The *function* of the acid will be discussed on page 283.

Manganous ions cannot exist in solution unless a corresponding number of negative ions is present. The same is true of the potassium ions. Since an excess of sulfuric acid was used in the reaction, it may be assumed that enough sulfuric acid is neutralized during the reaction to furnish sulfate ions for the positive ions mentioned.[1] The 2 potassium ions require 1 sulfate, and the 2 manganous ions 2 sulfate ions. Hence, 3 molecules of sulfuric acid are needed. The 3 molecules of sulfuric acid and the 5 of hydrogen sulfide supply 16 hydrogen ions not yet disposed of. Since everything is balanced except hydrogen and oxygen it may be assumed that 8 molecules of water are formed from the hydrogen ions. The final equation therefore reads:

$$\overset{7+}{2KMnO_4} + 5\overset{2-}{H_2S} + 3H_2SO_4 \rightarrow$$

$$\uparrow \quad 2\times 5\epsilon \quad = \quad 5\times 2\epsilon \quad \downarrow$$

$$\overset{2+}{2MnSO_4} + \overset{0}{5S} + K_2SO_4 + 8H_2O \qquad (5c)$$

The fact that the equation is really completely balanced justifies the assumption that hydrogen ion is used up as water.

One other illustration may be used to show how the writing of incomplete equations may be avoided in building up the final equation by the "electron" method. For this purpose the reaction between potassium dichromate and sulfurous acid in the presence of sulfuric acid may be used. (The different parts of the discussion are printed in different styles of type. Thus the additions to the equation made as a result of the discussion which is printed in **small boldface type** are indicated in the equation by characters in **small boldface type,** etc.) The valence number of chromium in the dichromate is 6+; the final product is chromium ion, Cr^{+++}. Each of the 2 chromiums therefore takes up 3 electrons. The sulfurous acid goes over to sulfuric acid; the

[1] In writing these equations, the scheme of writing the highly ionized substances as ions has not been followed. To have done so would have filled the equations with so many symbols that confusion might have resulted. The student is to bear in mind that of all the salts and highly ionized acids only very small amounts are present as molecules. In fact these substances may be completely dissociated.

sulfur in changing from a valence number of 4+ to 6+ gives up 2 electrons:

$$\overset{2\times 6+}{K_2Cr_2O_7} + 3H_2\overset{4+}{S}O_3 + 4H_2SO_4 \rightarrow$$

$$2\times 3\epsilon = 3\times 2\epsilon$$

$$\overset{3+}{Cr_2}(SO_4)_3 + 3H_2\overset{6+}{S}O_4 + K_2SO_4 + 4H_2O \quad (6)$$

To make the number of electrons lost equal to that of those taken up 3 H_2SO_4 must be used for 2 chromiums, that is for one $K_2Cr_2O_7$. Hence, $2Cr^{+++}$ and $3H_2SO_4$ are obtained.

The chromium ions cannot exist free, but must be counterbalanced by 3 sulfate ions, and the 2 potassium ions require 1 sulfate. Hence $4H_2SO_4$ are required. There are now 14 hydrogens on the left and only 6 on the right, hence $4H_2O$ will be required on the right. The equation is now balanced.[1]

Reactions in which the Oxidizing Agent also Acts as an Acid.—When strong acids like sulfuric or nitric acids are used as oxidizing agents, they may fulfill the functions of both oxidizing agent and acid. This is illustrated in the reaction between concentrated sulfuric acid and zinc, in which hydrogen sulfide and zinc sulfate are formed. The valence number of sulfur changes from 6+ to 2− and that of the zinc from zero to 2+. The oxidizing agent takes up 8 electrons and the reducing agent gives up 2. This is indicated in the incomplete equation:

$$\overset{6+}{H_2S}O_4 + 4\overset{0}{Zn} \rightarrow \overset{2-}{H_2S} + 4\overset{2+}{Zn} \quad (7a)$$

$$8\epsilon = 4\times 2\epsilon$$

The zinc ions cannot be formed unless there are negative ions to pair with them. Sulfuric acid is always used in excess in suffi-

[1] Obviously the $3SO_4^{=}$ ions resulting from oxidation of H_2SO_3 might have been used in this equation to supply negative ions for the potassium and chromic ions. By doing this, the equation becomes simplified to:

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

When one is learning to write equations of this sort it is best to keep the changes of the reducing and oxidizing agents clearly in mind and for this reason the longer equation has been given.

cient amount so that there are enough sulfate ions present for this purpose. $4Zn^{++}$ require $4H_2SO_4$, and this may be indicated in the equation:

$$\overset{6+}{(4+1)H_2SO_4} + \overset{0}{4Zn} \rightarrow \overset{-2}{H_2S} + \overset{2+}{4ZnSO_4} + 4H_2O \qquad (7b)$$

$$\uparrow 8\epsilon \quad = \quad \downarrow 4\times 2\epsilon$$

The $4H_2O$ have been added to balance the hydrogens, as has been amply described in previous examples. Prefixing the sum, 4 + 1, instead of simply using the number 5 before the symbol for the sulfuric acid, expresses the experimental fact that only 1 molecule of sulfuric acid is reduced to hydrogen sulfide, and that the remaining four act only as an acid to furnish negative ions for the zinc ions formed.[1] When the student has become thoroughly conversant with the balancing of such equations he may discontinue the use of this more elaborate form, but until he has gained considerable experience, he should continue to keep the number of molecules of acid which function as oxidizing agent separate from the number of those which function purely as acid. To make sure that he understands the scheme used, he should explain how every number in the following equation was obtained and what each represents.

$$\overset{0}{Cu} + (1+1)\overset{6+}{H_2SO_4} \rightarrow \overset{2+}{CuSO_4} + \overset{4+}{SO_2} + 2H_2O \qquad (8)$$

$$\downarrow 2\epsilon \quad = \quad \uparrow 2\epsilon$$

Reactions in which the same Substance Reacts as Oxidizing and as Reducing Agent.—Substances which may act both as oxidizing and as reducing agents have already been encountered. In such cases 1 molecule of the substance may oxidize another molecule of the same substance. This type of reaction occurs when sodium sulfite is heated (page 263). The products are

[1] The function of the acid will be more precisely explained in a later paragraph (page 283). It is to be noted that hydrogen sulfide is actually obtained in this reaction only if the zinc is merely moistened with concentrated sulfuric acid so that the hydrogen sulfide can escape without passing through the acid. If the gas passes through the acid, the hydrogen sulfide and sulfuric acid react to give sulfur and sulfur dioxide.

sodium sulfate and sodium sulfide. Evidently the valence number of some of the sulfur atoms changes from 4+ to 6+ while the valence number of others changes from 4+ to 2−; in other words those molecules which act as reducing agent lose 2 electrons each, while those which act as oxidizing agent take up 6 electrons each:

$$\overset{4+}{Na_2SO_3} \rightarrow \overset{6+}{Na_2SO_4} + \overset{2-}{Na_2S} \qquad (9)$$

2ϵ 6ϵ

(In this equation the first arrow represents the change in valence number corresponding to the formation of sodium sulfate on the other side of the equation and the second arrow represents the change in valence number for the formation of the sodium sulfide.) In order to equalize the number of electrons lost and taken up, three sodium sulfites must act as reducing agent for each one which acts as oxidizing agent:

$$(3+1)\overset{4+}{Na_2SO_3} \rightarrow 3\overset{6+}{Na_2SO_4} + \overset{2-}{Na_2S} \qquad (9a)$$

$3\times 2\epsilon = 6\epsilon$

An Alternative Method of Balancing Equations for Reactions of Oxidation and Reduction.—In using the scheme described for balancing equations for oxidation and reduction reactions, it is necessary to assign a definite positive valence number to some specific atom in compound ions like sulfate, permanganate and so on, and to assume that in all of these ions the oxygen is 2 negative. This positive valence number probably has not the same significance as the positive valence in simple ions such as sodium ion (see pages 260 and 367), and for this reason it is desirable to show that essentially the same scheme may be employed without making these assumptions. In equation (4), for example, the sulfate ion goes over into sulfide and oxygen ions:[1]

$$SO_4^{=} \rightarrow S^{=} + 4O^{=} \qquad (10)$$

On the left side of the equation there are two negative charges on all of the ions present; on the right side there are ten. To account for the

[1] Oxygen ions must be assumed to be present in any aqueous solution. They react almost completely with water according to the equation:

$$O^{=} + H_2O \rightarrow 2OH^{-}$$

appearance of the additional 8 electrons it must be assumed that, in the reaction, the sulfate takes up 8 electrons. This same conclusion was reached by assuming that the valence number of sulfur changed from 6+ to 2− (equation 4*b*). The balancing of the equation may therefore proceed just as before.

The Function of Acids in Oxidation and Reduction Reactions.—Substances like permanganates, chromates, nitrates, sulfates, and many other oxidizing agents are much more effective in acid than in neutral or in alkaline solutions. It used to be said that the function of the added acid is to liberate the hydrogen compound of the oxidizing or of the reducing agent. That this interpretation is incorrect, at least in most cases, is readily made clear. Potassium dichromate in neutral solution is practically unaffected by the addition of potassium iodide, but a little acid immediately causes the following reaction to take place:

$$\overset{2\times6+}{K_2Cr_2O_7} + 6\overset{1-}{K}I + 7H_2SO_4 \rightarrow$$

$$\overset{2\times3\epsilon}{\uparrow} \quad = \quad \overset{6\times1\epsilon}{\downarrow}$$

$$\overset{2\times3+}{Cr_2(SO_4)_3} + 3\overset{0}{I_2} + 4K_2SO_4 + 7H_2O \qquad (11)$$

It was formerly thought that the effect of the sulfuric acid is to liberate either dichromic acid ($H_2Cr_2O_7$) or hydriodic acid. But both of these acids are highly ionized; a solution containing them both consists largely of dichromate ions, iodide ions, and hydrogen ions. A solution of potassium dichromate and potassium iodide consists essentially of dichromate ions, iodide ions, and potassium ions. According to the earlier interpretation the only change made is the addition of hydrogen ions, and the interpretation therefore merely says that adding an acid causes the reaction to proceed because the acid (i.e., hydrogen ion) is added. This is obviously no explanation at all.

The modern interpretation of oxidation and reduction permits a real explanation of the function of the acid. As is shown by equation (11), the oxidizing agent, $K_2Cr_2O_7$, takes up 3 electrons for each chromium atom. The formation of chromium ion $(Cr)^{+++}$ and of oxygen ion is shown in the equation:

$$6\epsilon + Cr_2O_7^{=} \rightarrow 2Cr^{+++} + 7\,O^{=} \qquad (11a)$$

Addition of hydrogen ions (i.e., of an acid) removes the oxygen ions by forming water, and allows the reaction to proceed to the right—in other words allows the dichromate ion to function as an oxidizing agent by taking up electrons.

Forecasting the Products of Oxidation and Reduction.—Chemical equations, to be reliable, must always be a record of experimentally determined facts, and schemes for balancing equations cannot take the place of laboratory investigations of reactions. A reasonably good prediction of what might occur in a reaction is, nevertheless, often of considerable value. It may enable a chemist to solve a problem of scientific or of practical interest rapidly, since it may be the means of avoiding many unsuccessful attempts. Even a beginner, trying to become acquainted with what is already known rather than to discover new facts, will find the making of forecasts interesting and useful. One of the best aids in remembering a reaction is to try to foretell what will happen, and then to corroborate the guess by looking the reaction up. But the student must always bear in mind that the prediction is not enough; the corroboration is the really important part.

With experience, a considerable amount of skill may be acquired in making such forecasts. In ionic double decompositions, an understanding of the factors which influence equilibrium is of the greatest service, as has been shown in Chapters XV and XVI. There are also certain fundamental facts and modes of reasoning which permit the prediction of the course of oxidation and reduction reactions. It is important to know the usual valence numbers of elements and the changes which they commonly undergo. For example, permanganates are almost invariably reduced to manganous salts in strong acid solutions; in other words, the valence number changes from 7+ to 2+.[1] Chromates are nearly always reduced to salts of trivalent chromium, a reaction which involves a change of valence number from 6+ to 3+. Sulfate may be reduced to sulfur dioxide, to free sulfur or to sulfides. In the first case, the valence number of sulfur changes from 6+ to 4+, in the second, from 6+ to 0 and in the third from 6+ to 2−.

[1] In alkaline solutions, permanganates are more likely to be reduced to manganese dioxide in which the valence of manganese is 4+.

The factors determining which of several possible stages of reduction is reached in a given reaction are illustrated as follows. The sulfate ion need take on only 2 electrons to be reduced to sulfur dioxide, and it might be expected that a moderately weak reducing agent, which does not give up its electrons very readily, would bring about this reaction. In this way the reaction of copper on concentrated sulfuric acid can be accounted for (see page 281). Zinc, on the other hand, gives up electrons very readily, and it might therefore force as many electrons on the sulfur as the latter is capable of acquiring. It actually reduces sulfuric acid to hydrogen sulfide (see page 281).[1] In the same way, the difference in the behavior of concentrated sulfuric acid toward hydrobromic acid and toward hydriodic acid may be interpreted. Bromide ion has a considerable tendency to retain its electrons; for this reason it reduces concentrated sulfuric acid only to sulfur dioxide:

$$\overset{1-}{2HBr} + \overset{6+}{H_2SO_4} \rightarrow \overset{0}{Br_2} + \overset{4+}{SO_2} + 2H_2O \text{ [2]} \qquad (12)$$

$$\downarrow \quad\quad \uparrow$$

$$2\times 1\epsilon \;=\; 2\epsilon$$

[1] It is interesting, at this point, to attempt to explain why dilute sulfuric acid reacts with zinc to give hydrogen, while the concentrated acid gives hydrogen sulfide. When hydrogen is obtained, the essential reaction is:

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2$$

Hydrogen ions do not readily take up electrons. But dilute sulfuric acid is a very slow oxidizing agent (see page 269), and therefore does not take up the electrons as fast as the zinc releases them. For this reason they must go to the hydrogen. In concentrated sulfuric acid, the sulfate ion acts very readily as an oxidizing agent, and the electrons from the zinc are taken up by the sulfate rather than by the hydrogen. It is conceivable that metals which are more active reducing agents than zinc, might give up electrons even more rapidly than they can be taken up by sulfate in concentrated sulfuric acid; in such a case the formation of both hydrogen sulfide and hydrogen might be expected. Cases of this type will be discussed in connection with the reactions of nitric acid on magnesium.

This explanation is manifestly incomplete because it does not make clear why sulfuric acid in dilute solutions acts as an oxidizing agent so much more slowly than in concentrated solution. Probably in the latter both the dehydrating action of sulfuric acid, and the effect of the high concentration of hydrogen ions (see page 283) are important in increasing the speed of oxidations.

[2] In dilute solution this reaction is reversed.

Iodide ion, on the other hand, gives up its extra electron quite readily and therefore reduces the sulfuric acid to hydrogen sulfide:

$$\overset{1-}{8HI} + \overset{6+}{H_2SO_4} \rightarrow \overset{0}{4I_2} + \overset{2-}{H_2S} + 4H_2O \qquad (4)$$

$$8 \times 1\epsilon = 8\epsilon$$

EXERCISES

(1) (*a*) What are the electronic changes involved in the reaction between bromine and an aqueous solution of hydrogen sulfide? The products of the reaction are sulfur and hydrogen bromide. (*b*) Show how to balance the equation by the method developed in this chapter.

(2) What is the principle of the method developed in this chapter for the balancing of oxidation and reduction equations?

(3) (*a*) In the reaction between sulfur dioxide and bromine in aqueous solution, which substance must be the reducing agent and which the oxidizing agent? (*b*) What are the probable products of the reaction? (Bear in mind that sulfur dioxide reacts with water before bromine is added.) (*c*) Balance the equation. In all of the problems of this chapter, indicate as in the text how the equation is balanced.

(4) Balance the equation for the reaction between concentrated sulfuric acid and silver. The products are sulfur dioxide and silver sulfate. Use the method given on page 280.

(5) What valence numbers may be assigned to each element in the following compounds, the mode of ionization of which is indicated in the usual way: $H_3(PO_4)$, $H_3(AsO_3)$, $H(NO_3)$, $H_2(SnO_3)$, $H(ClO_2)$, $H(ClO_3)$, $H(ClO_4)$?

(6) Show how the method for balancing oxidation and reduction equations may be applied to work out equations 5, 6, and 7 on page 262.

(7) Balance the equation for the reaction of potassium permanganate and sodium chloride in the presence of dilute sulfuric acid. The reaction was used as a method for preparing chlorine.

(8) Balance the equation for the preparation of bromine by the action of manganese dioxide on a bromide in the presence of dilute sulfuric acid.

(9) Explain why sodium sulfite may act either as an oxidizing or a reducing agent. Under what conditions does it act in both capacities?

(10) (*a*) Explain why concentrated sulfuric acid is reduced to sulfur dioxide by hydrogen bromide, and to hydrogen sulfide by hydrogen iodide. (*b*) If, in the latter reaction, enough of the concentrated sulfuric acid were present so that the hydrogen sulfide liberated would pass

through a considerable quantity of sulfuric acid, what secondary products would be obtained? (*c*) Write the equations for the reactions involved in (*b*).

REFERENCES

HILDEBRAND—Principles of Chemistry, Chapter XV.
STIEGLITZ—Qualitative Chemical Analysis, Vol. I, pages 251–257 and 287–294.

In reading these references, bear in mind that the older terminology, "gain or lose positive charges" is equivalent to the statement "lose or gain electrons," and that "gain or lose negative charge" is equivalent to "gain or lose electrons."

CHAPTER XIX

NITROGEN, THE ATMOSPHERE, AND THE RARE GASES

The compounds of nitrogen are among the most important substances with which the chemist has to deal. Ammonia and nitric acid among the inorganic compounds, the dyes and explosives in the field of organic chemistry, or the proteins of living matter need only be mentioned to make this evident. Nitrogen itself, however, is very inactive, as a brief study of its properties will demonstrate, and one of the important problems of chemistry is to enable men to convert atmospheric nitrogen into products which are absolutely essential to human welfare. Before taking up the various solutions which have been proposed for this problem, it is necessary to review the sources of elementary nitrogen, and the substances associated with it in nature.

The Preparation of Nitrogen.—The only source to be considered for the commercial preparation of elementary nitrogen is air, of which nitrogen constitutes approximately 78 per cent by volume. To remove the oxygen, the air is passed over heated coke or coal, and the resulting oxides of carbon are removed. Copper may be used in place of the carbon. The resulting copper oxide is reduced to copper, and used over again. An entirely different method consists in the fractional distillation of air, already described in connection with the preparation of oxygen. The nitrogen obtained by these processes is not pure, but contains so little impurity that it can be used for most commercial purposes. For the preparation of nitrogen on the small scale, the method employing copper may be used.

Pure nitrogen is prepared from nitrogen compounds rather than by removal of the oxygen from air. Ammonia yields nitrogen when passed over hot copper oxide:

$$2NH_3 + 3CuO \rightarrow N_2 + 3H_2O + 3Cu \qquad (1)$$

Another method, very convenient when a steady stream of nitrogen is desired, is to heat an aqueous solution of ammonium nitrite.[1] Decomposition occurs according to the equation:

$$NH_4NO_2 \rightarrow N_2 + 2H_2O \qquad (2)$$

Physical Properties of Nitrogen.—Nitrogen condenses to a colorless liquid at about $-195°$ and solidifies at $-214°$. It is evident from these data that the molecules of nitrogen exert but little attractive force on one another. The density of the gas, 1.2506 at 0°, 760 mm., agrees with the formula N_2. At 0°, 760 mm., 100 volumes of water dissolve but 2.4 volumes of the gas.

Chemical Properties of Nitrogen.—Nitrogen combines directly with very few substances. When lithium, calcium, magnesium, boron, silicon or titanium are heated in nitrogen they combine with it to form nitrides. For the reaction with magnesium the equation is:

$$3Mg + N_2 \rightarrow Mg_3N_2 \qquad (3)$$

A mixture of aluminium with carbon, when heated to a very high temperature in nitrogen, yields aluminium nitride. Nitrogen reacts at high temperatures with calcium carbide to form the industrially important compound, cyanamide. Under special conditions, to be described later, it combines with hydrogen and with oxygen; in the electric arc it reacts slightly with carbon.

Active Nitrogen.—When a very high voltage discharge is passed through nitrogen at low pressures, a curious glow is observed just after the discharge has ceased. At the same time, the nitrogen becomes very reactive. It combines with phosphorus, sodium, mercury, sulfur and other elements with which ordinary nitrogen does not react appreciably, and enters into many other unusual reactions. This "active form" of nitrogen rapidly reverts to ordinary nitrogen, and the "after glow" mentioned above is supposed to be associated with the change of active to ordinary nitrogen. The energy expended in making

[1] Gentle heat is required to start the reaction, but heat is generated as the action proceeds, and the mixture must later be cooled to prevent too violent action. Instead of ammonium nitrite, a mixture of ammonium chloride and sodium nitrite is usually used.

the active nitrogen is too great to permit the use of the process for practical purposes, but considerable interest is connected with the phenomenon. In it an explanation of the extraordinary inertness of ordinary nitrogen may be found, on the assumption that the active nitrogen consists of nitrogen atoms, and that the ordinary nitrogen molecules (N_2) are unusually stable.[1]

The Atmosphere.—Although nitrogen and oxygen constitute approximately 99 per cent by volume [2] of normal air, some of the components present in minor amounts are nevertheless of great importance in some of the natural phenomena in which air is concerned. **Carbon dioxide** comes chiefly from the decay of animal and vegetable matter, and from the normal respiration of living beings.[3] By virtue of its ability to combine with oxides and thus to form carbonates, of which many minerals are composed, it has affected the constitution of the earth's crust; by virtue of its ability to displace weaker acids (such as silicic acid) from their salts, it has contributed to the mineralogical transformations which are an important phase of the earth's history. Water, saturated with carbon dioxide, converts many insoluble carbonates into soluble bicarbonates, and is thus a very important factor in erosion. Plants make use of carbon dioxide to build up sugars, and thus not only furnish food for animals, but prevent an undue accumulation of carbon dioxide in the atmosphere.

The importance of **water vapor** in climate and geological history is familiar to every student of elementary science. The amount of water vapor in the atmosphere bears an important

[1] An active modification of nitrogen, which is probably different from the one here described, has been obtained by passing a "silent" discharge through nitrogen. This modification may consist of molecules of N_3 analogous to ozone.

[2] The average composition of the air in volume per cent is as follows: nitrogen, 78.03 per cent; oxygen, 20.99 per cent; inert gases, 0.95 per cent; carbon dioxide, 0.03 per cent. These figures vary somewhat from time to time and from place to place and refer to air from which the moisture has been removed. The amounts of other components, such as sulfur dioxide and water vapor, are very variable but are always very small.

[3] The amount of carbon dioxide contributed to the atmosphere by the combustion of coal unquestionably influences the composition of the atmosphere in the neighborhood of large cities and great industrial centers, but it is too small to affect materially the composition of the atmosphere as a whole.

relation to bodily comfort, and its control is one of the problems of ventilation. Air sometimes contains small amounts of **ozone,** of **hydrogen peroxide** and of **oxides of nitrogen,** none of which is of importance so far as is known. **Sulfur dioxide, soot** and other substances result from human activities. Their influence is largely harmful. By increasing corrosion of metals and the deterioration of paints (used as protection for exposed surfaces of buildings) these by-products of modern life enormously increase the cost of living. Their influence upon the health of the dwellers in large cities, though not exactly understood, is unquestionably bad. One of the most important problems of science today is the prevention of atmospheric pollution.

The recognition of the fact that **air is a mixture** may almost be said to mark the beginning of chemistry as an exact science. Accurate analyses were required to perceive that the composition of air, even with respect to its most important components, oxygen and nitrogen, is not perfectly constant; a knowledge of the properties of both of these elements was essential before chemists could demonstrate that the properties of air are simply those of a mixture, since they can be calculated from the properties of the components; an exact understanding of the differences between substances and mixtures, and between elements and compounds had to be acquired before the nature of air could be comprehended. In the fixing of these concepts the study of the atmosphere has been of the utmost importance.

The Helium Family.—As the result of very accurate measurements, Rayleigh found that the weight of 1 liter of nitrogen, prepared from air and supposed to be pure, was 1.2572 grams at standard conditions, while the weight of the same volume of the gas, prepared from various nitrogen compounds averaged only 1.2506 grams. Since the samples of nitrogen prepared from a variety of compounds all showed the same density, the conclusion was drawn that nitrogen prepared in the usual way from air contains an impurity which is not removed in the course of purification.[1] Later Ramsay and Rayleigh proved that a residue

[1] It is interesting to note that some previous observations by Cavendish in 1785 really proved that an unknown gas exists in the atmosphere. The discovery of argon was not made until a century later.

is left after air is repeatedly passed over heated magnesium, which reacts with both oxygen and nitrogen. This residue was shown to consist largely of an hitherto unknown element which does not react with any known substance. Because of this inactivity it was named **argon**, from the Greek word for lazy. This discovery is an illustration of the unexpected results that may follow work of high accuracy.

It is well known that gases heated to incandescence or subjected to a spark discharge radiate light, which is shown by spectroscopic analysis to be made up of a large number of bright lines. Each element has certain spectral lines which characterize it perhaps more sharply than any other property. This fact has been utilized in determining the composition of the sun and other heavenly bodies. In 1868, Lockyer discovered certain lines in the spectrum of the sun, which could not be associated with any element then known on the earth. He assumed the existence of an unknown element which he called **helium**. As a result of the discovery of argon, Ramsay was investigating various little known gaseous substances. Among these was the gas given off by minerals containing uranium. It proved to have a spectrum identical with that of helium, which was thus discovered on the earth approximately thirty years after the spectroscope had revealed its presence in the sun. Helium, like argon, reacts with no known substance.[2]

The discovery of these two elements and their very unusual character led Ramsay to investigate the atmosphere with the utmost care. By fractionally distilling a large quantity of liquid air, he was able to isolate three other non-reactive elements which have been called **neon**, **krypton** and **xenon** (Greek for new, hidden, and stranger, respectively). Finally experiments with radioactive substances have led to the discovery of other gases of this

[2] Some recent examinations of the spectra of mixtures of hydrogen and helium and the comparison of these with the spectra of certain heavenly bodies, have led to the supposition that compounds of hydrogen and helium may exist. Although it is too early to draw any conclusions from these data, it seems likely that what occurs under the conditions of the experiments or in the heavenly bodies is a temporary association of hydrogen and helium atoms rather than the formation of a compound in the ordinary sense of the word.

type. To the one associated with radium, the names radium emanation, niton, and radon have been assigned by different investigators. The last one is favored at present. Of the six gases, argon has been found on the earth in largest amount, and xenon in the smallest. Radon is unstable and will be discussed more fully, as will helium, in connection with the phenomena of radioactivity. None of the gases is at all plentiful, although considerable quantities of helium are found in the natural gas which escapes from certain wells in Texas.

The physical properties of the elements are given in Table XIII.

TABLE XIII

	Atomic Weight	Melting Point, Degrees	Boiling Point, Degrees	Critical Temperature, Degrees
Helium	4.0	.....	−268.7	−268
Neon	20.2	−253	−233	−220
Argon	39.9	−188	−186	−117
Krypton	82.92	−169	−152	− 63
Xenon	130.2	−140	−109	+ 15

The exceedingly low critical temperatures of these elements, especially of the lighter ones, show that their atoms have very little attractive force for each other. This fact is in keeping with their inability to react with any known substance. In this connection, the problem of determining the atomic weight of the helium group gases may be mentioned. The atomic weight of an element has been shown to be the smallest weight of that element found in 22.4 liters of any of its gaseous compounds at standard conditions. But these elements form no compounds. It is possible, however, to determine the atomic weight of an element from the weight of 22.4 liters of the free gaseous element at standard conditions, if the number of atoms contained in 1 molecule of the elementary gas is known. Thus, since the hydrogen molecule consists of 2 atoms and the molec-

ular weight of hydrogen is 2.016, the atomic weight of hydrogen is one-half of this number. Now it has been shown mathematically that for gases the ratio of the specific heat at constant pressure to the specific heat at constant volume should have the value 1.67, irrespective of the chemical nature of the gas, provided that the gas consists of monatomic molecules. This value has been found for the ratio in the case of the inactive gases, and thus the weight of 22.4 liters of the substances at standard conditions may be taken as the atomic weight.

Only helium and argon have been discovered in amounts large enough to make it possible to utilize them in any way. Helium is employed in place of hydrogen to fill balloons. While helium is twice as heavy as hydrogen, its lifting power is only about 10 per cent less [1] than that of hydrogen. Helium is, of course, not inflammable, and that fact more than counterbalances the disadvantage of the somewhat smaller lifting power. Argon has been used to fill incandescent lamp bulbs. The presence of the inactive gas decreases the rate of evaporation of the filament. In spite of the fact that these elements are of so little use, they are very important from a theoretical point of view as will be seen in the discussion of the modern theories of atomic structure.

EXERCISES

(1) Show how the methods utilizing air and copper, and ammonia and copper oxide might be combined to make a continuous process. In answering, consider which substance is used up in each case.

(2) Considering the decomposition of ammonium nitrite to be a reaction in which a substance oxidizes and reduces itself, show how to balance the equation by the electronic method. The nitrogen atom of ammonium ion may be considered to be 3− and that of the nitrite ion 3+.

(3) List the chemical properties of nitrogen.

(4) What is active nitrogen and how is it prepared?

[1] The lifting power of a gas is determined by the difference between the density of the air and that of the gas. For hydrogen this difference is about 27 units, while for helium it is 25 units. The density of the air is taken as 29, that of hydrogen 2, and that of helium 4.

(5) What is the evidence that air is a mixture?

(6) Describe the discovery of argon and of helium.

(7) Suggest a method, different from that described in the text, for determining roughly the atomic weights of the inactive gases. (Use the equations developed on page 27.)

REFERENCES

LOWRY—Inorganic Chemistry (1922). Pages 361–376 contain a descriptive treatment of nitrogen and the atmosphere.

RAMSAY—The Gases of the Atmosphere (1902) discusses very interestingly and in non-technical language the influence exerted on chemistry by the study of the atmosphere. It leads up to and describes the discovery and properties of the inactive gases. The book is an excellent review of the history of theories of combustion.

FRIEND—Text Book of Inorganic Chemistry. Vol. III, Part I, Chapter VI (1924). This text, like Mellor's Treatise, is a large work, not quite complete but nearer completion than Mellor's. It is not so detailed as the latter, nor so well arranged, but is a valuable work of reference.

MAXTED—Ammonia and the Nitrides. Chapter VII describes the experiments leading to the discovery of active nitrogen and discusses its properties.

CHAPTER XX

COMPOUNDS OF NITROGEN WITH HYDROGEN AND WITH THE HALOGENS

The Ammonium Ion

Ammonia has been known and used for a very long time. It was formerly prepared by heating the horns and hoofs of animals and was known as " spirits of hartshorn," but its use has increased so much that this source of supply has ceased to be adequate. Other methods of manufacture have completely superseded the older one. Enormous quantities of ammonia, in the form of ammonium salts, are now used in fertilizers; aqueous solutions of the gas are employed in large quantities in chemical industry and in the laboratory, as well as in the household; the gas itself is the raw material in one of the important processes for the manufacture of nitric acid. Large refrigerating installations use ammonia in machines similar in principle to that described for the liquefaction of air. The reactions of ammonia are of unusual interest from a scientific point of view, and for all of these reasons the substance is worthy of rather detailed study.

The Commercial Production of Ammonia.—Soft coal contains approximately 1 per cent of nitrogen in the form of compounds of unknown character. A part of this nitrogen is converted into ammonia when the coal is heated out of contact with air, as in the manufacture of coke. In the old " bee-hive " type of coke ovens all of the ammonia, together with the valuable " coal tar " and other useful products, is lost. " By-product " coke ovens are designed to collect all of these wasted substances, and after this type of oven has completely replaced the older one, approximately 400,000 tons of ammonia will be obtained annually in the United States from coke manufacture. But even this large amount will not be enough to supply our needs.

The Haber Process.—Since nitrogen is so easily available and hydrogen can be obtained cheaply from water, the direct synthesis of ammonia from its elements would seem to be the simplest method for increasing the supply. But when hydrogen and nitrogen are mixed at ordinary temperatures no reaction whatever occurs. Rise of temperature, on the other hand, causes progressive decomposition of ammonia with absorption of heat, according to the equation:

$$24{,}000 \text{ calories} + 2NH_3 \rightleftarrows N_2 + 3H_2 \qquad (1)$$

Since 4 molecules of the mixture of nitrogen and hydrogen yield only 2 molecules of ammonia, increase of pressure drives the reaction to the left. In order to manufacture ammonia successfully by direct union of its constituent elements, the reaction should therefore be carried out at as low a temperature and as high a pressure as possible. In order to obtain a clear picture of the conditions, Haber actually determined the amount of ammonia obtainable in the reaction at various temperatures and pressures, as shown in the following table.[1]

TABLE XIV

SHOWING THE PER CENT OF A MIXTURE, CONSISTING OF 3 VOLUMES OF H_2 AND 1 VOLUME OF N_2, CONVERTIBLE INTO NH_3 AT VARIOUS TEMPERATURES AND PRESSURES

TEMPERATURE, °C.	PER CENT OF NH_3 AT			
	1 ATMOSPHERE	30 ATMOSPHERES	100 ATMOSPHERES	200 ATMOSPHERES
200	15.3	67.6	80.6	85.8
400	0.44	10.7	25.1	36.3
600	0.05	1.4	4.5	8.25
800	0.01	0.35	1.15	2.24

At ordinary pressure, the amount of ammonia obtainable increases very greatly as the temperature falls so that at room

[1] The actual equilibrium conditions were determined at a few high temperatures and from these data the possible yields at lower temperatures were calculated. The calculations are based on thermodynamic principles which cannot be explained here.

temperature the reaction should go almost to completion toward the formation of ammonia. But, as has already been pointed out, the reaction proceeds so slowly under these conditions that practically no combination occurs. Even at temperatures as high as 400° it is far too slow to be feasible as a method of manufacture. But once the possibilities in the reaction were known it became worth while to search for catalysts capable of speeding up the process to a point at which it might be practicable. It was finally found that iron, uranium, osmium, as well as other metals and mixtures of metals catalyzed the reaction sufficiently between 400 to 500°.[1] As is seen from the table, an appreciable yield of ammonia can be obtained only by the use of high pressures at these temperatures. The reaction is said to be carried out at approximately 200 atmospheres. Great difficulties were encountered in designing apparatus which would withstand these large pressures at the elevated temperatures, and would not allow the hydrogen to escape by diffusion. The ammonia formed in the reaction is removed from the mixture by condensation at low temperatures, and the residual gas is allowed to react again. The hydrogen and nitrogen must be pure, as the presence of oxygen makes the process dangerous to carry out, and other substances may " poison " the catalyst.

The Cyanamide and Other Processes.—When nitrogen is passed over calcium carbide, CaC_2, at about 1200° **calcium cyanamide** is obtained:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \qquad (2)$$

The cyanamide is sold under various trade names as a fertilizer, but may be converted into ammonia by the action of steam and dilute alkali:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3 \qquad (3)$$

[1] The exact composition of the catalyst used in the Haber process, and the details of construction of the apparatus employed were kept secret by the Germans during the World War. Not much has been disclosed since that time. Recently an announcement has been made that chemists working in the United States have discovered a catalyst active at lower temperatures, but here again few details are available. (See reference to Larson at the end of the chapter.)

A large plant for carrying out this process was constructed at Muscle Shoals, Alabama, during the World War but was never used. Cyanamide is now manufactured on the large scale in the United States.

Aluminium oxide, in the form of bauxite, reacts with carbon and nitrogen to give aluminium nitride and carbon monoxide. The nitride is converted into aluminium hydroxide and ammonia by means of heated sodium hydroxide. From the aluminium hydroxide metallic aluminium is manufactured. This process, invented by **Serpek,** has not been very successful, because the reaction goes relatively slowly even at high temperatures, and the reagents cause rapid deterioration of the reaction vessels.

For **laboratory preparation** (which need practically never be carried out because ammonia is purchasable almost everywhere) some ammonium salt is gently heated with slaked lime:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + CaCl_2 + 2H_2O \qquad (4)$$

Physical Properties of Ammonia.—Ammonia at ordinary temperatures is a colorless gas possessing a pungent odor. It boils at $-33.5°$ and freezes at $-78°$. Its critical temperature is about 133°, so that it can easily be liquefied by pressure at ordinary temperatures. When evaporated at its boiling point, the liquid absorbs 330 cals. per gram. This relatively large amount of heat accounts for the usefulness of ammonia as a refrigerant. The gas is extremely soluble in water: 1 volume of water dissolves nearly 1300 volumes of ammonia at 0°, and about 700 volumes at 20°.

Chemical Properties of Ammonia.—Ammonia is an **exceedingly weak acid** as is shown by the fact that the more active metals displace hydrogen from it. Thus liquid ammonia reacts with sodium to give sodium amide:

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2 \qquad (5)$$

All of the nitrides may be looked upon as salts of ammonia in which all of the hydrogen has been displaced. That ammonia is an extraordinarily weak acid is shown by the fact that even its

salts with strong bases, such as sodium amide or magnesium nitride, are completely hydrolyzed by water: [1]

$$NaNH_2 + HOH \rightarrow NaOH + NH_3 \qquad (6)$$

$$Mg_3N_2 + 6H_2O \rightarrow 2NH_3 + 3Mg(OH)_2 \qquad (6a)$$

For this reason the acid properties of ammonia are never observed in aqueous solutions or in the presence of moisture, and are therefore not important under ordinary conditions. But the dissociation of ammonia into hydrogen ions and a negative nitrogen ion shows that the nitrogen in the compounds is $3-$, a fact which is of interest in connection with some of its other reactions.[2] The acid properties of ammonia also affect the behavior of anhydrous liquid ammonia as a solvent, as was mentioned on page 240.

Ammonia, especially at higher temperatures, acts as a mild **reducing agent.** Its reaction with copper oxide in the preparation of nitrogen is an illustration. It reacts also with oxygen when heated, burning with a pale yellow flame, but it does not burn in air unless it is very dry. Nitrogen is the chief product of the combustion under these conditions, but if the reaction is carried out in the presence of a catalytic agent at lower temperatures nitric acid is obtained. Ammonia is oxidized by the halogens, giving nitrogen and the halogen acid.[3] In aqueous solution it is not readily oxidized by the more common oxidizing agents such as permanganates or chromates, and on this account is not usually classed as a reducing agent.[4]

[1] Reference to Table XI, page 234, in which the extent of hydrolysis of salts of various acids is given, will make clear how weak an acid ammonia is. Sodium cyanide is hydrolyzed only about 1 per cent in tenth normal solution, although hydrocyanic acid is a very weak acid. In the case of the salts of ammonia, hydrolysis is, however, favored by the fact that the ammonia is partially removed by the formation of ammonium ion. (See page 301.)

[2] Like any other acidic substance capable of yielding more than 1 hydrogen ion, ammonia dissociates most readily into H^+ and NH_2^-, but nitride ion, $N^{\equiv}$, must also exist.

[3] The products of these reactions when aqueous ammonia is used will be discussed in connection with the halogen compounds of nitrogen, page 304.

[4] Most oxidizing agents are employed in acid solutions. In such solutions, ammonia is practically completely removed by the formation of ammonium ion. This fact is partly responsible for the resistance of the ammonia to oxidation under these conditions.

The most important chemical property of ammonia is its ability to **unite with hydrogen ion and certain other positive ions,** such as silver, copper, nickel or cobalt ions. When ammonia is passed into a solution of hydrochloric acid, the acidity of the solution decreases until the solution becomes practically neutral. The hydrogen ion is evidently removed, and in its stead a new ion, the **ammonium** ion, appears.

$$H^+ + NH_3 \rightleftharpoons (NH_4)^+ \qquad (7)$$

The whole reaction is:

$$H^+ + Cl^- + NH_3 \rightleftharpoons NH_4^+ + Cl^- \qquad (7a)$$

When the solution is evaporated and the water (which keeps the positive ammonium ion separated from the negative chloride ion) is removed, the 2 ions become associated with each other in the white crystalline solid, ammonium chloride. In analogous fashion ammonia forms salts with practically all acids.

Ammonia **reacts also with water.** Water dissociates somewhat into hydrogen ions, and the ammonia combines with these to form ammonium ions. The hydroxide ion must therefore be left free to a certain extent as shown by the first part of the equation:

$$NH_3 + HOH \rightleftharpoons NH_4^+ + OH^- \rightleftharpoons NH_4OH \qquad (8)$$

The ammonium and hydroxide ions combine to a limited extent to form molecular **ammonium hydroxide.** Ammonium hydroxide is not as highly ionized as are the ammonium salts—it is, in other words, not a strong base. Aqueous solutions of ammonia are therefore used whenever a moderately weak base is needed.

Action of Bases on Ammonium Salts.—The reaction between ammonia and hydrogen ion is reversible. Any reagent which removes the hydrogen ion must therefore drive the reaction represented by equation (7) to the left. Hydroxide ions, added in excess, remove the hydrogen ions to form water, and therefore decompose ammonium salts into ammonia:

$$Na^+ + OH^- + (NH_4)^+ + Cl^- \rightarrow H_2O + NH_3 + Na^+ + Cl^- \qquad (9)$$

Since the sodium and chloride ions undergo no change, any strong base will act in analogous fashion with any ammonium salt.

Ammonium Hydroxide.—The formation of ammonium ion by the action of ammonia on water or on acids, shows that it is entirely unnecessary to assume the formation of ammonium hydroxide in order to interpret the reactions of solutions of ammonia or of ammonium salts. Evidence obtained at very low temperatures shows that ammonia actually forms the compound $NH_3 \cdot H_2O$, which is probably the hypothetical ammonium hydroxide.[1] Furthermore, there is an advantage in considering ammonium salts as salts of the moderately weak base, ammonium hydroxide, for it permits the reactions of these salts toward water and toward bases to be classified with those of the salts of other weak bases.

Decomposition of Ammonium Salts by Heat.—Ammonium salts are in most respects very similar to sodium and potassium salts, particularly to the latter. Two exceptions may be noted. Ammonium salts are slightly hydrolyzed:

$$NH_4^+ + Cl^- + HOH \rightleftharpoons NH_4OH + H^+ + Cl^- \qquad (10)$$

This reaction goes only very little to the right because ammonium hydroxide is only a moderately weak base.[2] In the second place, ammonium salts are all readily decomposed by heat. In most cases, the products are ammonia and the acid from which the salt is derived. Thus:

$$NH_4Cl \rightarrow NH_3 + HCl \qquad (11)$$

and

$$NH_4H_2PO_4 \rightarrow NH_3 + HPO_3 + H_2O \ ^3 \qquad (12)$$

[1] The existence of ammonium hydroxide was demonstrated by the freezing point curves of solutions of ammonia in water. A minimum in the freezing point corresponds to the composition mentioned. This method, however, shows only that the compound exists as a solid, and does not prove its existence in solution.

[2] As has been pointed out above, this reaction may be interpreted even more simply without the assumption that ammonium hydroxide is formed. This is shown by the equation:

$$NH_4^+ + Cl^- \rightleftharpoons NH_3 + H^+ + Cl^-$$

This equation is nothing more than a statement that reaction (7*a*) is slightly reversible.

[3] H_3PO_4 is first formed. It decomposes into $HPO_3 + H_2O$.

But if the acid is an oxidizing agent, oxidation products of ammonia may be formed. Ammonium nitrite (page 289) and ammonium dichromate yield nitrogen:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O \qquad (13)$$

Ammonium nitrate gives nitrous oxide:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad (14)$$

Union of Ammonia with other Positive Ions.—Silver hydroxide is very slightly soluble in water. It dissolves, however in solutions of ammonia. From the equation:

$$AgOH \downarrow \rightleftarrows Ag^+ + OH^-$$

it is obvious that silver hydroxide can be dissolved only by the removal of the silver ion or the hydroxide ion. Since the addition of ammonia to water increases the amount of hydroxide ion, the silver ion must be the one which is removed. This occurs as a result of the reaction:

$$Ag^+ + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ \qquad (15)$$

The reaction is reversible, for when an acid is added to the solution, hydrogen ions combine with the ammonia to form ammonium ions, and thus drive the reaction to the left. Many other ions of the metallic elements combine with ammonia in this way, and the matter will receive further discussion. The reaction of ammonia with silver ion is quite analogous to that with hydrogen ion, except that in the former case each of the positive ions unites with 2 molecules of ammonia.[1] These ions are called **complex ions.** They may perhaps differ from compound ions such as sulfate and nitrate ion only in stability; possibly a more fundamental difference exists. (See pages 572–575.)

[1] It is interesting to note that the number of ammonia molecules combined with the positive ion is equal to twice the charge on the ion, except in the case of the complex ion of hydrogen and ammonia, which to bring out the analogy, may be written $H(NH_3)^+$. $Ag(NH_3)_2^+$, $Cu(NH_3)_4^{++}$ and $Co(NH_3)_6^{+++}$ are examples. This rule is not absolutely rigid, but for each metal ion capable of uniting with ammonia at all, there is at least one complex ion in agreement with the rule. The ammonium ion may be only an apparent exception, for it is well known that ammonium salts are capable of taking up additional ammonia. No adequate explanation for the rule is known.

Other Compounds of Nitrogen and Hydrogen.—Two other compounds of nitrogen and hydrogen are known. **Hydrazine,** N_2H_4, is like ammonia in many respects but is a much stronger reducing agent. It is used extensively in organic chemistry. **Hydrazoic** acid, HN_3, is an exceedingly explosive substance. It is a strong acid, an oxidizing agent, and also a reducing agent.

Halogen Compounds of Nitrogen.—Aqueous solutions of ammonia, treated with chlorine or with hypochlorous acid (HOCl), yield chlorine compounds of nitrogen. When just enough sodium hypochlorite is added to furnish 1 gram atomic weight of chlorine for each ammonia, **monochloramine,** NH_2Cl, is obtained; with an excess of hypochlorite or by the action of an excess of chlorine on ammonium chloride, **nitrogen trichloride,** NCl_3, is formed. Both substances are oily liquids which are extremely reactive and exceedingly explosive. They are completely hydrolyzed by water. Nitrogen trichloride has been the subject of considerable discussion. Since the trichloride is prepared from ammonia, which contains negative nitrogen, and hypochlorous acid, which contains chlorine with a positive valence number, it might be looked upon as a compound of negative nitrogen and positive chlorine. But chlorine has a great tendency to become negative chloride ion, and nitrogen is capable of forming compounds in which it has the valence number 3+. This line of reasoning has led to the idea that there might be another nitrogen trichloride with the formula $N^{+++}Cl_3^-$. All efforts to prepare this other substance have hitherto failed, nor is there a very great likelihood that they will be successful.—Iodine likewise acts on aqueous solutions of ammonia, but the product obtained has the formula, $NI_3 \cdot NH_3$, and is a brown solid. When dry, it explodes upon the slightest shock—a touch with a feather is sufficient to induce the explosion. Bromine and fluorine form no simple compounds with nitrogen; both yield nitrogen when they act on ammonia or on ammonium salts.[1]

EXERCISES

(1) Give a brief description of three processes for the preparation of ammonia on the large scale.

(2) Explain why the synthesis of ammonia from the elements should be carried out at as low a temperature and as high a pressure as possible. Use Le Chatelier's rule.

(3) What difficulties are encountered in synthesizing ammonia at low temperatures?

[1] The compounds N_3Cl and N_3I, which are related to hydrazoic acid, are known.

(4) Why is ammonia useful as a refrigerant?

(5) (*a*) What is the evidence that ammonia possesses acid properties? (*b*) What is the evidence that it is an exceedingly weak acid? (*c*) Why are the acid properties usually not enumerated among the properties of ammonia?

(6) Because of what property does ammonia act as if it had basic properties? Explain with a concrete illustration, for example the action of ammonia on aqueous solutions of hydrochloric acid.

(7) (*a*) What evidence is there that the action between ammonia and hydrogen ion is reversible? (*b*) Explain the behavior of ammonium salts toward strong bases, such as sodium hydroxide, on the basis of the reversibility discussed in (*a*).

(8) Explain why silver hydroxide is soluble in aqueous solutions of ammonia.

(9) In the text, the solvent action of aqueous solutions of ammonia on silver hydroxide was explained as due to the free ammonia present. Why would it not have been correct to ascribe the action to ammonium ion which must also be present?

(10) Why is it possible for ammonia to be a reducing agent, according to the hypothesis of reduction used in this text?

(11) Write the equations for the thermal decomposition of (*a*) ammonium nitrate, (*b*) ammonium nitrite, (*c*) ammonium chloride.

REFERENCES

Knox—Fixation of Atmospheric Nitrogen (1921) is a small book but contains a relatively large amount of information well presented. Section II deals with the synthesis of ammonia and describes some of Haber's original experiments on the equilibria involved. Section III deals with nitrides and cyanamide.

Kempton—Industrial Nitrogen (1922) is a book of the same scope as the preceding.

Pring—The Electric Furnace (1922) contains an excellent section on nitrogen products. Pages 145–152 deal with the synthesis of ammonia, and pages 136–143 with cyanamide.

Larson and Collaborators have published a series of papers in Chemical and Metallurgical Engineering, Vol. **26**, which deal with various phases of the Haber process. Both experimental and plant apparatus are described. Many of the articles are very technical; the one on pages 588–593 gives details of the experimental large scale plant.

(See also references to Chapter XXI.)

CHAPTER XXI

OXIDES AND OXYGEN ACIDS OF NITROGEN

NITROGEN forms an unusually large number of compounds with oxygen—nitrous oxide, N_2O, nitric oxide, NO, nitrogen trioxide, N_2O_3, nitrogen dioxide, NO_2, nitrogen tetroxide, N_2O_4, and nitrogen pentoxide, N_2O_5. All of the oxides are more or less readily decomposed by heat. The valence number [1] of nitrogen in these compounds varies in steps of one from 1+ to 5+. This fact is of great importance in formulating their reactions and those of nitric acid.

Nitrous Oxide.—Since the valence number of the nitrogen in nitrous oxide is 1+, it is theoretically possible to prepare the substance by the reduction of any nitrogen compound in which nitrogen has a higher positive valence number. From a practical point of view only nitric acid need be considered. It is reduced by a mixture of stannous chloride and hydrochloric acid to nitrous oxide:

$$\overset{5+}{2HNO_3} + \overset{2+}{4SnCl_2} + 8HCl \rightarrow \overset{1+}{N_2O} + \overset{4+}{4SnCl_4} + 5H_2O \quad (16)$$

$2 \times 4\epsilon = 4 \times 2\epsilon$

A more common method is the decomposition of solid ammonium nitrate by heat:

$$\overset{3-}{N}H_4\overset{5+}{N}O_3 \rightarrow N_2O + 2H_2O$$

$4\epsilon = 4\epsilon$

The reaction begins at approximately 170°; heat is liberated and if the solid is heated too rapidly an explosion may result.

[1] The reason why nitrogen exhibits so many valence numbers is not known. The relationship of valence number and the mode of union of the atoms in the molecules is discussed on page 367.

Nitrous oxide decomposes rather readily into the elements; a splinter of wood, sulfur or phosphorus burns in the gas even more readily than in air, since the oxide on decomposition yields a mixture of nitrogen and oxygen, richer in the latter than air. The chief use of the substance is as the well-known anesthetic, laughing gas.

Nitric Oxide.—Nitric acid is reduced to nitric oxide by any one of a large number of reducing agents. For example, the oxide is obtained by the action of copper on **dilute** nitric acid (1 : 1) or of ferrous sulfate on warm, dilute nitric acid:

$$\overset{0}{3Cu} + (6+2)\overset{5+}{H}NO_3 \rightarrow 3Cu(\overset{5+}{N}O_3)_2 + 2\overset{2+}{N}O + 4H_2O \quad (17)$$

$3 \times 2\epsilon = 2 \times 3\epsilon$

$$6\overset{2+}{Fe}SO_4 + 2\overset{5+}{H}NO_3 + 3H_2SO_4 \rightarrow 3\overset{3+}{Fe}_2(SO_4)_3 + 2\overset{2+}{N}O + 4H_2O \quad (18)$$

$6 \times 1\epsilon = 2 \times 3\epsilon$

Although either of these reactions may be used in the laboratory, the direct union of nitrogen and oxygen is the only important **industrial method for the preparation of nitric oxide.** This reaction is one of the steps in the manufacture of nitric acid from air. Nitrogen and oxygen, like nitrogen and hydrogen, do not react at ordinary temperatures and nitric oxide, like ammonia, decomposes when heated. In the case of nitric oxide, the temperature required for appreciable decomposition is considerably higher than in the case of ammonia. But the most important difference between the behavior of nitric oxide and ammonia in this respect is that in the decomposition of the latter, heat is absorbed, whereas evolution of heat accompanies the decomposition of nitric oxide:

$$2NO \rightarrow N_2 + O_2 + 43{,}200 \text{ cals.} \quad (19)$$

According to Le Chatelier's rule, therefore, rise in temperature ought to favor the formation of nitric oxide rather than its decomposition. The contradiction between theory and fact is not a real one. Even at ordinary temperatures nitric oxide has a **tendency** to decompose, but the velocity of the reaction is too

small to be appreciable. Rise of temperature increases the reaction velocity. The speed of the reaction at various temperatures has been estimated as shown in the following table, in which the speed is stated in terms of the time required for the decomposition of one-half of any given quantity of nitric oxide.

TABLE XV

TIME REQUIRED FOR HALF DECOMPOSITION OF NITRIC OXIDE

Temperature....	1273°	1773°	2173°	2373°
Time.....	81.6 years	1.26 days	2 minutes	5 seconds

Rise of temperature, on the other hand, affects the equilibrium in accordance with the heat of reaction and Le Chatelier's rule, for at very high temperatures decomposition of nitric oxide is not complete, and nitrogen and oxygen actually unite. The following table gives the per cents of a mixture of equivalent amounts of nitrogen and oxygen which combine at various temperatures.

TABLE XVI

PER CENT OF N_2 AND O_2 WHICH UNITE AT VARIOUS TEMPERATURES

Temperature..	1773°	2773°	3473°	4473°
Per cent combination....	0.1 per cent	1.8 per cent	4.4 per cent	10 per cent

Several conclusions concerning the preparation of nitric oxide from the elements may be drawn from these data. In the first place, it is obvious that search for a catalytic agent is a waste of time. A catalyst at ordinary or moderately high temperatures would only decompose any nitric oxide formed. In the second place, the reaction must be carried out at extraordinarily high temperatures. Finally, after the nitric oxide has been formed at the high temperature, the reaction mixture must be cooled very rapidly, in order that the nitric oxide may not again decompose spontaneously with appreciable velocity.

It is not easy to meet all of these conditions for manufacturing nitric oxide from air, but a number of practical methods have been devised as the result of many years of experimentation. All of them employ the electric arc to attain the very high tempera-

ture needed. The differences between the various processes lie chiefly in the methods for rapidly cooling the reaction mixture. The first practical method was invented in the United States. It was not very successful because of the high cost of electricity and the rapid deterioration of the apparatus. At present, the reaction is carried out chiefly in Norway, where water power is abundant and cheap, and where the product can be economically disposed of. The **Badische** process employs a discharge through a tube over 20 feet long. The air enters in such a way that it passes through the discharge and strikes against the cooled walls of the vessel. In the **Birkeland-Eyde** process, rapid cooling of the gases is accomplished by spreading the arc into a circular brush discharge between electromagnets. The arc extends over a considerable area, but it is thin and makes and breaks many times, so that the gases are rapidly removed from the zone of high temperature.[1] By the use of these devices, yields from 1 to 2.5 per cent are obtained in practice. It is obvious, from the low yield, that the processes can be used only where power is very cheap.

The methods for the synthesis of ammonia and of nitric oxide have been discussed at length, not only because of the intrinsic importance of the products, but chiefly to show how an understanding of the principles underlying chemical reactions leads to successful experiments. The search for a suitable catalyst in the ammonia reaction has taken many years, but the time was well spent because theoretical considerations had demonstrated beyond doubt that catalysts could accomplish the desired result. Search for catalysts in the nitric oxide reaction, on the other hand, would have been a waste of time. At present, chemical science is engaged in a theoretical study of the nature of catalysts. Solution of that problem may enable chemists of the future to pick out catalysts for reactions according to some definite principle, instead of having to employ the slow, blind method of trial and error which still is the only method known.

[1] The yields obtained in the various processes are somewhat higher than can be explained solely by the temperature to which the air is exposed. Probably the electrical discharge itself favors the reaction, perhaps by partly dissociating the elementary molecules or by forming one of the more active modifications of nitrogen.

The comparison of ammonia and nitric oxide brings out several other points of considerable importance. In the presence of a suitable catalytic agent, nitric oxide should decompose completely at ordinary temperatures, whereas ammonia should be completely stable. Nevertheless, in the absence of an efficient catalyst, a small rise in temperature causes much more complete decomposition of ammonia than of nitric oxide, since the latter decomposes at an almost immeasurably slow rate even at 1000°. It is therefore impossible to judge from the decomposition temperatures which of two substances is the more stable.

For cases like that of nitric oxide, the term **metastable** has been introduced. A substance or a mixture is metastable if its continued existence in a given condition is determined by the extreme slowness of a chemical change rather than by the fact that no chemical change is possible.[1] Statements with regard to the relative stability of two substances are necessarily limited to definite conditions; ammonia is stable at ordinary temperatures and nitric oxide metastable, whereas at very high temperatures ammonia is unstable and nitric oxide stable.[2]

The Properties of Nitric Oxide.—Owing to the extreme slowness with which nitric oxide decomposes even at fairly high temperatures, substances like wood, which do not burn with very hot flames, cease to burn when introduced into an atmosphere of the oxide. Phosphorus burns with a flame hot enough to

[1] In order to determine whether a substance is stable or merely metastable, complete knowledge of the energy changes accompanying its formation is necessary. The problem is one of thermodynamics and cannot be taken up in this text. In general, substances formed with the evolution of a large amount of heat are stable at ordinary temperatures, while substances formed with the absorption of a considerable amount of heat are unstable or metastable. This is not an absolute rule, since the heat of a reaction is not a measure of its tendency to take place. The two factors are frequently found to parallel each other—a fact that has led to erroneous conclusions in the past. The possibility of being led astray by this rule is illustrated in the case of ammonia. Almost complete decomposition occurs at 500°, although heat is absorbed in the reaction.

[2] This statement is based on the assumption that evolution of heat accompanies the formation of ammonia at whatever temperature the reaction is carried out. There is some evidence to indicate that a reversal of heat effect occurs in the ammonia equilibrium at very high temperatures.

dissociate the oxide, and on this account continues to burn in this gas even more readily than in air.[1] In the course of the reaction, phosphorus is oxidized to phosphorus pentoxide (P_2O_5) and nitric oxide is reduced to nitrogen. In accordance with the fact that the valence number of nitrogen in nitric oxide is 2+, **nitric oxide not only acts as an oxidizing agent,** as in the reaction just cited, but it may act also as a **reducing agent.** When it is passed through a concentrated solution of nitric acid, nitrogen dioxide is formed:

$$\overset{5+}{4HNO_3} + \overset{2+}{2NO} \rightarrow \overset{4+}{6NO_2} + 2H_2O \qquad (20)$$

$$\uparrow \quad \downarrow$$

$$4 \times 1\epsilon = 2 \times 2\epsilon$$

It is also very readily oxidized by the oxygen of the air. Nitric oxide is colorless; the admixture of air at once produces the reddish-brown color of the dioxide. This reaction may be used as a qualitative or quantitative test for oxygen:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (21)$$

Only one other reaction of nitric oxide need be taken up. With aqueous solutions of ferrous sulfate **nitric oxide reacts to form the compound** $(Fe \cdot NO)SO_4$. As indicated by the formula the nitric oxide and the ferrous ion unite to form a complex ion, which is dark brown.[2] The color is so intense that the reaction may be used as a test for nitric acid or nitrates. The latter are reduced to nitric oxide by ferrous sulfate in sulfuric acid solution. The nitric oxide then unites with excess of the ferrous sulfate to produce the brown compound. The substance $(Fe \cdot NO)SO_4$ is readily decomposed into ferrous sulfate and nitric oxide by slight elevation of temperature; for this reason the reagents must be kept cool in making the nitrate test.

Nitrogen Tetroxide and Dioxide.—Two methods for the preparation of nitrogen dioxide have already been described in the reactions of nitric oxide with air and with nitric acid. (Equations 20 and 21.) It is most commonly obtained in the

[1] This reaction may be a direct action of nitric oxide, since the rate of decomposition is very slow even at the temperature of the phosphorus flame.

[2] In the presence of very concentrated sulfuric acid the color is cherry red.

laboratory by the action of metals of intermediate activity, such as copper or tin, on **concentrated** nitric acid, or by the thermal decomposition of nitrates, except those of ammonium and the alkali metals.

$$2Cu(NO_3)_2 \rightarrow 4NO_2 + 2CuO + O_2 \qquad (22)$$

When cold the substance is a pale yellow liquid (boiling point 22°) which freezes to an almost pure white solid at 10.5°. When heated it changes to a dark, reddish-brown gas. Rise in temperature above 160° causes the color to disappear again. These color changes are due to two reactions. At low temperatures the molecular weight corresponds to the formula N_2O_4, or **nitrogen tetroxide,** which is a colorless or slightly yellowish substance. As the temperature is raised, the pressure increases much more rapidly than it should according to the gas laws, and at 156° is twice that expected. N_2O_4 evidently decomposes, giving 2 molecules of a new substance **nitrogen dioxide,** NO_2, to which the dark brown color is due. Continued rise in temperature causes further decomposition, yielding colorless nitric oxide and oxygen. The decomposition is appreciable (about 5 per cent) at 180°, but is not complete until the temperature is raised above 600°. All of the reactions are readily reversible, and may be represented by the equations:

$$\underset{\text{light yellow}}{N_2O_4} \overset{22\text{–}156^\circ}{\rightleftharpoons} \underset{\text{dark brown}}{2NO_2} \overset{156\text{–}620^\circ}{\rightleftharpoons} \underset{\text{colorless}}{2NO + O_2} \qquad (23)$$

At room temperatures, the gas is therefore a mixture of NO_2 and N_2O_4.[1, 2] The one substance rapidly goes over into the other. Any substance which reacts with N_2O_4 removes it, and therefore drives the reaction completely to the left; any substance which reacts with NO_2 removes this component, and causes the first reaction of equation (23) to go to the right. For

[1] Considerable confusion exists in the nomenclature of these substances. In the days before a scientific basis for making formulae had been developed, nitric oxide (NO) was called nitrogen dioxide. Although this name should be reserved for NO_2, some writers still use it in the older sense.

[2] Liquid nitrogen tetroxide is quite dark in color at room temperature. It unquestionably contains considerable NO_2 in solution.

this reason it is impossible to determine which reactions are to be ascribed to the one form and which to the other. Equations may therefore be written with either formula, and the names nitrogen dioxide and tetroxide are used interchangeably.

The reactions of nitrogen tetroxide with water are of great importance. If the water is cold, the primary products are nitric and nitrous acids:

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2 \qquad (24)$$

But if the temperature is raised, or if the solution becomes concentrated, the nitrous acid decomposes: [1]

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \qquad (25)$$

The nitrogen tetroxide of course dissolves again and the final products of the action, under these conditions, are nitric oxide and nitric acid:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (26)$$

If sodium hydroxide is used in place of the water, the first of these reactions, (24), alone occurs, except, of course, that sodium nitrite and sodium nitrate are formed instead of the free acids.

The process of obtaining nitric oxide from the air may be combined with the reactions of nitric oxide and nitrogen dioxide to prepare **nitric acid from the atmosphere.** The nitric oxide formed in the arc always contains an excess of oxygen. When the mixture is cooled to below 600° combination of the two substances with the formation of nitrogen dioxide begins and is complete at 156°. The latter may then be mixed with water giving nitric acid and nitric oxide. The nitric oxide may again be treated with an excess of air, and the newly formed nitrogen dioxide again absorbed in water. By successive treatments nearly all of the nitric oxide is converted into nitric acid. Sometimes **nitrates** and **nitrites** are prepared by passing the nitrogen dioxide into solutions of sodium or calcium hydroxide.

Nitrogen Trioxide and Pentoxide.—Nitrogen trioxide, or nitrous anhydride, is obtained by cooling to −21° or lower temperatures, an equimolecular mixture of nitric oxide and nitrogen tetroxide. The resulting

[1] The reaction $3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$ also takes place directly.

product is a deep blue liquid which when evaporated dissociates almost completely into the substances from which it is prepared:[1]

$$N_2O_3 \rightleftarrows NO + NO_2 \qquad (27)$$

Nitrogen pentoxide may be obtained by the action of phosphorus pentoxide on very concentrated nitric acid:

$$2HNO_3 + P_2O_5 \rightarrow N_2O_5 + 2HPO_3 \qquad (28)$$

It consists of white crystals which may be purified by sublimation at slightly elevated temperatures. It is very easily decomposed into nitrogen tetroxide and oxygen.

Neither nitrogen pentoxide nor trioxide is of practical importance, since both are so readily decomposed. They are the anhydrides of nitric and nitrous acids respectively.

The Oxygen Acids of Nitrogen

Manufacture of Nitric Acid.—Sodium nitrate in the form of **Chile saltpeter** was for a long time the only, and is today the chief raw material in the manufacture of nitric acid. The material is found in enormous deposits in the dry portions of South America lying near the boundary of Chile and Peru. The origin of the deposits is not understood, although it is generally assumed to be of organic nature. Nitric acid is obtained from the nitrate by the action of concentrated sulfuric acid:

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4 \qquad (29)$$

Both acids are highly ionized, but the action nevertheless proceeds to the right because of the greater volatility of nitric acid. The distillation of the latter from the mixture is carried out at reduced pressure in order to operate the process at a lower temperature, and thus to prevent decomposition of the nitric acid as much as possible. Iron retorts are employed, but the acid must be condensed in glass tubes and the acid collected in earthenware vessels.

As a result of the success of the Haber process, ammonia is now available in amounts sufficient for the production of nitric acid. For this purpose, a mixture of ammonia and air, to which

[1] When nitrogen trioxide is exceedingly dry, decomposition is much less nearly complete than with ordinary N_2O_3.

an excess of oxygen has been added, is passed over electrically heated platinum gauze, which catalytically hastens the reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (30)$$

The heat developed keeps the platinum at the correct temperature, and artificial heating is unnecessary except at the beginning of the process. The excess of oxygen oxidizes the nitric oxide to the tetroxide when the reaction mixture cools. The conversion of the latter to nitric acid is effected by absorption in water, as in the nitric oxide process. The success of this method, known as the **Ostwald process,** depends on careful attention to details. Very exact temperature regulation is required. This is brought about by controlling the composition of the original mixture and the rate at which the gases pass over the catalyst.

The manufacture of nitric acid from **nitric oxide,** obtained by union of the **oxygen and nitrogen of the atmosphere** has already been described. (Page 313.)

Physical Properties of Nitric Acid.—The pure acid is a colorless liquid miscible in all proportions with water. It boils at 86° and freezes at −47°. It fumes strongly on contact with moist air. Addition of water to the acid raises the boiling point to 120.5°; further addition of water lowers it again. The acid of constant boiling point contains 68 per cent of the acid, and is the concentrated acid of commerce.

Chemical Properties of Nitric Acid.—Pure nitric acid and the very concentrated solutions in water, although apparently stable when kept in the dark, decompose slowly when exposed to light according to the equation:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2 \qquad (31)$$

A part of the nitrogen tetroxide remains dissolved in the acid and gives it a yellowish color. The decomposition is hastened by rise in temperature. For this reason, distillation of nitric acid at ordinary pressure causes progressive decomposition, and repeated distillation finally leads to the solution of constant boiling point. The pure acid also decomposes into nitrogen pentoxide and water, but in order to make this reaction go forward the water formed must be removed by a dehydrating agent like phosphorus pentoxide (equation 28).

Some of the most important properties of nitric acid are exhibited in its **behavior toward organic substances.** Only two illustrations will be cited. **Glyceryl nitrate,** $C_3H_5(NO_3)_3$, better known as **nitroglycerine,** the high explosive, is prepared by the action of a mixture of concentrated nitric and sulfuric acids on glycerine ($C_3H_5(OH)_3$). Similarly **gun cotton** is made by the action of the same mixture on the cellulose in cotton. From these substances **dynamite** and **other explosives** are manufactured. Dynamite, for example, is made by dissolving gun cotton in nitroglycerine. If, in the nitration of cellulose, the action is not allowed to go to completion, partially nitrated cellulose is obtained. This product is worked between rollers with a mixture of camphor and alcohol, and forms a viscous solution which, on evaporation of the alcohol, leaves behind the transparent colorless **celluloid.**

The second type of reaction of nitric acid on organic substances is illustrated in the formation of **nitrobenzene** ($C_6H_5NO_2$) by the action of nitric and sulfuric acids on benzene (sometimes called benzol). This reaction is one of the early steps in converting coal tar into useful substances, for from the nitrobenzene aniline is made, and from the latter large numbers of dyes, drugs and so on are manufactured. The development of the "coal tar industry" is one of the most fascinating chapters in the history of chemistry. To those who are not already familiar with its outlines, the reading of some of the references cited at the close of the chapter on carbon compounds is strongly recommended.

Finally nitric acid is a **strong acid** and a powerful **oxidizing agent** even in dilute solution. It will be recalled that sulfuric acid acts effectively as an oxidizing agent only in concentrated solution.

Nitric Acid as an Oxidizing Agent.—The action of nitric acid as an oxidizing agent is one of the most complicated which the beginner in chemistry meets. Reduction of the acid [1] may lead to the formation of any one of the compounds of nitrogen in which its valence number is less than 5+, i.e., to any of the oxides enumerated in the preceding section (except nitrogen pentoxide)

[1] It must not be forgotten that the oxidizing agent is reduced and the reducing agent oxidized in oxidation and reduction reactions.

or to nitrogen, hydroxylamine [1] or ammonia. The nature of the reducing agent determines to a great extent which of these products is obtained, but the temperature at which the reaction is carried out and the concentration of the acid also are important. Catalytic agents, present as impurities in the acid or in the reducing agent or formed during the course of the action, frequently determine which of several possible reactions actually occurs. Thus ordinary nitric acid readily dissolves both copper and silver, but nitric acid perfectly free from oxides of nitrogen is said to attack neither of them. Finally the nitric acid or the water in the reaction mixture may enter into secondary reactions with the products. Suppose, for example, that nitrogen tetroxide is formed in the primary reduction of a dilute solution of nitric acid. Part of it dissolves in the water to give nitrous and nitric acids. The nitrous acid may then decompose to give nitric acid and nitric oxide.

Owing to these complications, statements found in the chemical literature with regard to many of the reactions of nitric acid are contradictory. Nevertheless the following generalizations (in which only the main reactions are taken into consideration and the minor products neglected) will be found of value in correlating the important facts.

(1) **The More Active the Reducing Agent the Greater Will be the Change in the Valence Number of the Nitrogen.**—In illustrating this statement the action of dilute nitric acid must be chosen in order to avoid complications due to secondary actions of the acid on the reaction products. In accordance with the generalization just made, the action of weak reducing agents (such as silver or mercury among the metals, and sulfur, phosphorus and carbon among the non-metals) leads primarily to the formation of nitrogen tetroxide, a change of valence number from 5+ to 4+:

$$\underset{\downarrow 1\epsilon}{Ag} + (1+1)\underset{\uparrow 1\epsilon}{HNO_3} \rightarrow AgNO_3 + NO_2 + H_2O \qquad (32)$$

$$\underset{\downarrow 6\epsilon = 6\times 1\epsilon}{S} + 6\underset{\uparrow}{HNO_3} \rightarrow H_2SO_4 + 6NO_2 + 2H_2O \qquad (33)$$

[1] See page 324.

If the nitric acid is very dilute, a secondary reaction takes place between the nitrogen tetroxide primarily formed and the water present:

$$3NO_2 + H_2O \rightarrow NO + 2HNO_3 \qquad (26)$$

Consequently even the weakest reducing agents, if they react at all, must give some nitric oxide when the acid is dilute, but this may be considered a secondary product.[1]

Somewhat more active reducing agents than those just discussed give nitric oxide with dilute nitric acid, a change in valence number from 5+ to 2+. The method of preparing nitric oxide by the action of copper or of ferrous sulfate on nitric acid (equations 17 and 18, page 307) are illustrations of this case.[2]

Still more active reducing agents, like stannous chloride in hydrochloric acid or tin itself, may give nitrous oxide or nitrogen. The action of stannous chloride has already been discussed (equation 16, page 306); that of tin on dilute acid may be written:

$$\underset{\downarrow}{5Sn} + (10 + 2)\underset{\uparrow}{HNO_3} \rightarrow N_2 + 5Sn(NO_3)_2 + 6H_2O \qquad (34)$$
$$5\times 2\epsilon \quad = \quad 2\times 5\epsilon$$

Nitrous oxide and nitrogen are usually obtained mixed with other reduction products, and the equations given are therefore incomplete records of the reactions.

Reducing agents as strong as zinc reduce the dilute nitric acid to ammonium nitrate—a change in valence number of nitrogen from 5+ to 3−:

$$\overset{0}{\underset{\downarrow}{4Zn}} + (9 + 1)\overset{5+}{\underset{\uparrow}{HNO_3}} \rightarrow 4\overset{2+}{Zn}(NO_3)_2 + \overset{3-}{NH_4}NO_3 + 3H_2O \qquad (35)$$
$$4\times 2\epsilon \quad = \quad 8\epsilon$$

[1] Students should not only make sure that they understand the balancing of the reaction equations and the sequence of reactions, but should attempt to balance equations for all of the reducing agents mentioned in order to review the method used.

[2] There seem, however, to be some unusual features about the reaction of copper on nitric acid. An acid somewhat stronger than the 1 : 1 mixture used in the preparation of nitric oxide is said to give nitrous oxide and even nitrogen. The presence of copper nitrate formed in the course of reaction seems to exert a catalytic effect which has some rôle in the formation of these products.

Finally the most active reducing agents not only reduce the nitrogen to a valence of 3−, but also reduce the hydrogen ion to elementary hydrogen. For this case, two equations should be written as illustrated for magnesium:

$$\overset{0}{4Mg} + (9+1)\overset{5+}{H}NO_3 \rightarrow 4Mg(NO_3)_2 + \overset{3-}{N}H_4NO_3 + 3H_2O \quad (36)$$

$4 \times 2\epsilon = 8\epsilon$

$$\overset{0}{Mg} + 2\overset{1+}{H}NO_3 \rightarrow Mg(NO_3)_2 + \overset{0}{H_2} \quad (37)$$

$2\epsilon = 2 \times 1\epsilon$

All of the metals above magnesium in the electromotive series (page 215) behave in similar fashion.

(2) **The More Dilute the Nitric Acid, the Greater, in General, is the Change in the Valence Number of the Nitrogen.**—A number of illustrations of this generalization have already been encountered. Copper with diluted nitric acid gives nitric oxide—a change in valence number from 5+ to 2+—while with concentrated nitric acid nitrogen tetroxide is obtained, corresponding to a change of only one in the valence number. It is, of course, possible to ascribe the difference in the two cases to a secondary action of the concentrated nitric acid in oxidizing the nitric oxide primarily formed (page 311), but it is just as correct to consider that the reaction occurs in one step:

$$\overset{0}{Cu} + (2+2)\overset{5+}{H}NO_3 \rightarrow Cu(NO_3)_2 + \overset{4+}{2}NO_2 + 2H_2O \quad (38)$$

$2\epsilon \quad 2 \times 1\epsilon$

Similarly zinc with more concentrated nitric acid may give nitrogen or nitrous oxide; and with very concentrated acid nitric oxide and nitrogen tetroxide may be obtained instead of ammonium nitrate, the product of the action of dilute acid.[1]

Evidently the maximum reduction (i.e., the maximum change in the valence number of the nitrogen which a given reducing

[1] Statements concerning the action of zinc on nitric acid are also conflicting. Some writers state that nitrous oxide is obtained from the most dilute solutions.

agent may bring about), is usually exhibited in the action toward the dilute acid. When more concentrated acid is used any reduction product representing a change in valence number less than that observed with dilute acid may be expected. The stronger the acid, the smaller the change in the valence number.

(3) A few additional points will aid the student in systematizing the numerous reactions of nitric acid.

(*a*) Neither nitrogen trioxide nor nitrous acid has been listed among the reduction products of nitric acid. Both are too unstable to be of importance in this connection. Nitrous acid is occasionally found in small amounts, when weak reducing agents and dilute solutions are used.

(*b*) Non-metals are usually oxidized to oxides or to oxygen acids, as illustrated in the cases of sulfur, carbon and phosphorus which give sulfuric acid,[1] carbon dioxide and orthophosphoric acid (H_3PO_4) respectively. Metals are usually oxidized to nitrates. A few form such weak hydroxides that their nitrates are completely hydrolyzed, as illustrated in the action of tin on concentrated nitric acid:

$$Sn + (4 + 4)HNO_3 \rightarrow Sn(NO_3)_4 + 4NO_2 + 4H_2O \quad (39a)$$

$$Sn(NO_3)_4 + 3H_2O \rightarrow H_2SnO_3 + 4HNO_3 \quad (39b)$$

Since there is no decisive evidence that stannic nitrate is obtained in the reaction it is better to write the equation in one step:[2]

$$\overset{0}{Sn} + 4H\overset{5+}{N}O_3 \rightarrow \overset{4+}{H_2Sn}O_3 + 4\overset{4+}{N}O_2 + H_2O \quad (39)$$

$$\downarrow 4\epsilon \quad = \quad \uparrow 4 \times 1\epsilon$$

(*c*) Positive ions which exist in more than one valence stage may be oxidized from the lower to the higher stage by nitric acid. Thus ferrous ion is oxidized to ferric ion as in the action of ferrous sulfate or nitrate on nitric acid (equation 18, page 307). Stannous ion is oxidized to stannic ion as shown in one of the methods

[1] Sulfur dioxide may be obtained with the less concentrated nitric acid.

[2] Note the difference in the behavior of dilute and concentrated nitric acid on tin. Moderately dilute acid gives appreciable quantities of nitrous oxide and nitrogen, very dilute acid gives ammonium nitrate, and concentrated acid, nitrogen tetroxide.

for the preparation of nitrous oxide (equation 16 page 306). For this reason nitric acid, unless quite dilute, will oxidize the metals to the " ic " salts rather than to the " ous " salts. Thus concentrated nitric acid gives stannic acid with tin, whereas the dilute acid gives stannous nitrate.

Aqua Regia.—Gold and platinum are not attacked by nitric acid but are dissolved by a mixture of nitric and hydrochloric acids, known as aqua regia. The fundamental change when gold and concentrated nitric acid are brought together is oxidation of gold to auric ion and reduction of the nitric acid to nitrogen tetroxide, as shown in the equation:

$$\underset{\substack{\downarrow \\ 3\epsilon}}{Au} + 3HNO_3 \rightleftarrows \underset{\substack{\uparrow \\ 3\times 1\epsilon}}{Au^{+++}} + 3NO_2 + 3OH^- \qquad (40a)$$

Since gold does not act on nitric acid, this equilibrium is evidently normally displaced far to the left, even in the presence of an excess of hydrogen ions which remove the hydroxide ions. In order to drive the reaction to the right, it is necessary to remove the gold ions also. This is accomplished by the hydrochloric acid, the chloride ions of which unite with auric ions to form the very stable complex ion, $AuCl_4^-$. The whole reaction may be written:

$$Au + 3HNO_3 + 4HCl \rightarrow HAuCl_4 + 3NO_2 + 3H_2O \qquad (40b)$$

Platinum is dissolved by aqua regia because the complex ion $PtCl_6^=$ is formed. In the reaction chlorine also is liberated because concentrated nitric acid oxidizes hydrochloric acid, but chlorine seems not to play a rôle of any importance in dissolving these metals.[1]

Nitrates.—Nitrates are characterized by their great solubility. All nitrates are fairly readily decomposed by heat. The nitrates of the alkali metals give nitrites:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2 \qquad (41)$$

Those of the less active metals are decomposed to the oxide:

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2 \qquad (42)$$

[1] Aqua regia is a very complex mixture. It contains the two acids, free chlorine, the compound nitrosyl chloride, NOCl, and dissolved oxides of nitrogen.

The alkaline earth metals at low temperatures decompose into the nitrites; at higher temperature the latter break down into the oxide and nitrogen tetroxide. Lithium, in this respect, may be classed with alkaline earth metals. The decomposition of ammonium nitrate into nitrous oxide and water has already been described. (Page 306.)

Nitrates differ from nitric acid in that they are not readily reduced in aqueous solution. A general explanation of this phenomenon has already been given on page 283, in connection with the similar difference between dichromates and dichromic acid, but a repetition at this place will bring out another interesting confirmation of the view there presented. Zinc reduces nitric acid to ammonium nitrate but does not act on nitrates:

$$\overset{0}{4Zn} + \overset{5+}{NO_3^-} \rightleftarrows 4Zn^{++} + N^{\equiv} + 3O^{=} \qquad (43a)$$

$$\downarrow \quad \uparrow$$

$$4 \times 2\epsilon = 8\epsilon$$

The equilibrium in the reaction is normally displaced far to the left and in order to drive the reaction to the right some of the reaction products must be removed. This is accomplished by any acid. Hydrogen ion combines with the nitride ion to form ammonia and ammonium salts, and with oxygen ion to form water. Consequently the reaction goes forward in acid solution. But the reaction could just as well be driven toward the right by removing the zinc ion. Sodium hydroxide converts the latter into the zincate ion, $ZnO_2^=$. In strongly alkaline solutions zinc actually reduces nitrates to ammonia:

$$4Zn + NaNO_3 + 7NaOH \rightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O \qquad (43b)$$

This reaction is used as a test for nitrates in cases in which the ferrous sulfate test is not feasible.

Nitrous Acid and the Nitrites.—The preparation of nitrites by decomposition of alkali metal nitrates at elevated temperatures has already been described. (Page 321.) Lead is often added to the nitrate to remove the oxygen formed, and thus hasten the reaction. When nitrites are treated with dilute sulfuric acid the solution turns slightly bluish owing to the liberation of **nitrous acid,** HNO_2. The latter is unstable, decomposing into water and the trioxide, which at once suffers further decomposition into nitric oxide and tetroxide. In dilute solutions the acid decomposes slowly enough to permit a study of its properties.

The liberation of nitrous acid from its salts by sulfuric acid shows that it is a **weak acid.** It may act as a **reducing agent** because the valence number of nitrogen may change from 3+ in nitrous acid to 4+ or 5+. An illustration is its reaction with potassium permanganate:

$$\overset{3+}{5HNO_2} + \overset{7+}{2KMnO_4} + 3H_2SO_4 \rightarrow$$

$$\downarrow 5\times 2\epsilon \quad = \quad \uparrow 2\times 5\epsilon$$

$$\overset{5+}{5HNO_3} + K_2SO_4 + \overset{2+}{2MnSO_4} + 3H_2O \qquad (44)$$

This reaction is used to distinguish nitrates from nitrites. But nitrous acid may act also as an **oxidizing agent** because the valence number of the nitrogen may change to a value less than 3+. Thus it is reduced by ferrous sulfate to nitric oxide. The reaction is quite similar to that of nitric acid with ferrous sulfate. The same brown compound, $(Fe\cdot NO)SO_4$, is formed and for this reason the reaction cannot be used as a test for nitrates unless nitrites are absent. Nitrous acid also oxidizes potassium iodide:

$$\overset{1-}{2KI} + \overset{3+}{2KNO_2} + 2H_2SO_4 \rightarrow 2K_2SO_4 + \overset{2+}{2NO} + \overset{0}{I_2} + 2H_2O \qquad (45)$$

$$\downarrow 2\times 1\epsilon \quad = \quad \uparrow 2\times 1\epsilon$$

The iodine is liberated rapidly; nitric acid, on the other hand, acts very slowly with potassium iodide. It is found, in general, that nitrous acid oxidizes substances more rapidly than does nitric acid. Nevertheless the latter is the stronger oxidizing agent as is shown by the fact that it oxidizes certain substances which nitrous acid does not attack.

Nitrites and nitrous acid obtained from them are extensively used in chemistry, as for example in the dye industry.

Hyponitrous Acid.—Reduction of nitrous acid by sodium amalgam results in the formation of the sodium salt of hyponitrous acid, $H_2N_2O_2$. It decomposes spontaneously into nitrous oxide:

$$H_2N_2O_2 \rightarrow N_2O + H_2O \qquad (46)$$

Nitrous oxide is therefore sometimes called the anhydride of hyponitrous acid, but this is a matter purely of form since the reverse of reaction 46 does not take place.

Hydroxylamine.—Another compound containing nitrogen, hydrogen and oxygen is hydroxylamine, NH_2OH. It is obtained by the reduction of nitric acid by tin or by electrolysis. It is also prepared by the action of nitrites on acid sulfites. It is a reducing agent and a valuable reagent in organic chemistry. In contrast to the other oxygen-hydrogen compounds of nitrogen mentioned, hydroxylamine is not an acid, but like ammonia and hydrazine combines with hydrogen ion and therefore acts like a base.

EXERCISES

(1) Give a method of preparation and the most important properties of each of the oxides of nitrogen, except nitrogen trioxide.

(2) Explain why, although nitric oxide is more stable at high temperatures than at low ones, rise of temperature nevertheless causes decomposition.

(3) Explain why use of catalysts would be harmful, rather than beneficial, in the preparation of nitric oxide at low temperatures.

(4) Explain why nitric oxide, prepared at high temperatures, must be rapidly cooled in the process of manufacture.

(5) Contrast the difficulties encountered in the synthesis of ammonia and that of nitric oxide.

(6) What is a metastable substance?

(7) Describe all of the changes which occur when nitrogen tetroxide is heated and give equations for the reactions.

(8) Explain why it is impossible to determine which reactions of a mixture of nitrogen dioxide and tetroxide are due to the one and which to the other substance.

(9) Write the equations for the reactions of nitrogen tetroxide with water, and state under which conditions each occurs.

(10) Describe the method of making nitric acid from air.

(11) Name all of the methods described in this text, for converting the nitrogen of the air to useful products.

(12) List the important chemical properties of nitric acid, including at least one not mentioned directly in this chapter.

(13) Make a list of all of the possible reduction products of nitric acid. In a parallel column indicate whether the product mentioned in the first column would be obtained more easily with dilute or with concentrated nitric acid. In a third column state whether an active or an inactive reducing agent should be employed. In the fourth column of the table thus assembled, name a specific reducing agent which, with the acid mentioned in the second column, would give the product referred to.

(14) Write the equations for the most likely reaction of dilute nitric acid on each of the following substances. If two reactions are certain to occur, write both equations. Balance all equations by the electron method:

(*a*) copper; (*b*) tin; (*c*) zinc; (*d*) magnesium.

(15) Answer as in 14 for the action of concentrated nitric acid on:

(*a*) copper; (*b*) tin; (*c*) sulfur.

(16) Answer as in 14 for the action of nitric acid on:

(*a*) lead; (*b*) iron.

Since the action of these metals was not described in the text the answer must be based on the general criteria given, and on the relative activity of the metals in question and those discussed in the text.

(17) Explain why aqua regia is more effective than pure nitric acid in dissolving platinum.

(18) Write the equations for the thermal decomposition of: sodium nitrate, lead nitrate, ammonium nitrate.

(19) (*a*) What is the evidence that nitrous acid is a weak acid? (*b*) Write a reaction equation illustrative of the reducing properties of nitrous acid. Explain why it possesses such properties. (*c*) Answer as in (*b*) for the oxidizing properties of nitrous acid.

(20) (*a*) Devise a method for proving the presence of nitrous acid in solutions containing nitric acid. (*b*) Devise a method for destroying nitrous acid in a mixture with nitric acid without decomposing the latter. (*c*) Give a method of testing for nitric acid after the nitrous acid has been removed. Write equations for all reactions involved in all parts of this exercise.

REFERENCES

The three books cited in the References to Chapter XX deal also with the electrical processes for making nitric oxide and the catalytic oxidation of ammonia.

Rogers—Industrial Chemistry, Chapter V, describes the manufacture and uses of nitric acid.

Lowry—Inorganic Chemistry (1922). Pages 376–417 contain a survey of the properties of nitrogen compounds. The discussion is more descriptive than the one in this text.

Details about the action of nitric acid on various metals can be found in the works of reference (e.g., Mellor or Friend) often cited. They are given in connection with the descriptions of the properties of the metals.

CHAPTER XXII

THE PERIODIC SYSTEM

The existence of groups of elements of similar properties has long been recognized. The halogens, the alkali and alkaline earth metals may be cited as illustrations. Thus all of the halogens have a decided tendency to become univalent negative ions, they unite vigorously with metals, and form highly ionized hydrogen compounds and salts. Just as striking as the similarities are the gradations in properties observed when the elements of the group are compared with each other. Fluorine displaces chlorine, chlorine displaces bromine, and bromine displaces iodine. The variations in practically all of the other properties show the same order: hydrogen fluoride is the most stable, hydrogen iodide the least stable hydrogen compound of the four; fluorine acts most vigorously with the metals, with water, with many carbon compounds, while iodine reacts least vigorously. In the present state of our knowledge it is easy to recognize that the order of these elements with respect to their chemical properties is also the order of their atomic weights.

Döbereiner as early as 1829 had observed some relationships between the atomic weights of the elements and their chemical properties, but his observations did not lead to a system applicable to all the elements, because of the lack of a scientific basis for atomic weights.

The Periodic Law.—No progress was made along these lines until 1860. In that year an international congress was held for the purpose of unifying the conflicting notions about atomic weights. A brilliant exposition by Cannizarro of the advantages of Avogadro's law as a basis for the calculation of atomic weights caused our modern system to be generally accepted. Not long afterward (1863) Newlands, an English chemist, foreshadowed the

generalization now known as the periodic system, and in 1869 the Russian, Mendeléeff, and the German, L. Meyer, quite independently outlined the same idea.[1] Mendeléeff's conception and development of the principle were so much more complete and profound than those of the others that the real discovery has been credited to him. To use his own words, the **periodic law** thus discovered states that "**all of the properties of the elements, both physical and chemical, vary as a periodic function of their atomic weights.**"

The Mendeléeff Periodic Table.—Mendeléeff made the significance of the periodic law very clear by arranging the elements in a suggestive form of table. His method is indicated, although quite incompletely, as follows. The symbols of the first eight elements, beginning with helium,[2] are written in a horizontal row. For convenience, the atomic weight of each element is placed in parentheses after its symbol. Under each symbol is given the charge on the simple ion formed by the element. For carbon, which forms no simple ion, the valence numbers are used, and for nitrogen the maximum positive valence number is given in addition to the valence of the nitride ion. Of course Mendeléeff considered all of the properties of the elements, and not only the valence, but as the periodic table is considered more fully in later paragraphs, the following is sufficient for the present.

He(4.0)	Li(6.9)	Be(9.1)	B(10.9)	C(12.0)	N(14.0)	O(16)	F(19.0)
0	1+	2+	3+	4+, 4−	5+, 3−	2−	1−

The elements constitute a strikingly regular series; the positive valence increases by steps of one from 0 (helium) to 5+ (nitrogen), and the negative valence, beginning with carbon, decreases by steps of one. There are no duplications in valence to suggest that any of these elements should belong to a single group.

Now consider the next eight elements, again in the order of ascending atomic weights. In this row, the positive and negative

[1] In 1862 a Frenchman, deChancourtois, also made a contribution along the same lines. His ideas were much less clearly thought out, and included some incorrect notions.

[2] Helium and neon were not known to Mendeléeff. Likewise he did not distinguish between positive and negative valence. The discussion of the table has thus been somewhat modified from Mendeléeff's method to include the developments since his time.

valence numbers for silicon, which forms no simple ion, are given. The maximum positive valence number which phosphorus, sulfur and oxygen exhibit in compound ions are put down in addition to the valences of the simple ions.

Ne(20.2)	Na(23)	Mg(24.3)	Al(27)	Si(28.1)	P(31)	S(32.1)	Cl(35.46)
0	1+	2+	3+	4+, 4−	5+, 3−	6+, 2−	7+, 1−

The same regularity in valence change is again evident; the second series brings out the relationship even more clearly than the first one, for in the second there is a continuous increase in valence from 1+ to 7+. Although the valence alone is here considered, it is clear from previous discussions that the pairs, neon and helium, sodium and lithium, sulfur and oxygen, and chlorine and fluorine resemble one another closely in many other properties.

The next elements in order, argon (39.9), potassium (39.1), calcium (40.1) and scandium (45.3) fit very well under neon, sodium, magnesium and aluminium according to their valences and other chemical properties, as might be expected if this **periodic** arrangement of the elements based on atomic weight continues to hold true. But the elements after scandium are not closely related to the corresponding elements of the two preceding series. Titanium (48.1) is still quite similar to silicon. Vanadium (51) has a valence number 5+ in some of its compounds but is never 3−, chromium is 6+ in chromates but is never 2−, and manganese, although it shows the valence number 7+ in the permanganates, has valences different from those of chlorine in other compounds and is never 1−. Nor are vanadium, chromium, and manganese at all similar in their physical and chemical properties to phosphorus, sulfur and chlorine, as might be expected according to the findings in the first two series.

The Short and Long Series.—In order to account for the failure of vanadium, chromium and manganese to fit chemically with phosphorus, sulfur and chlorine, Mendeléeff suggested that the series beginning with argon is of a type different from the preceding ones. Not until krypton (82.9) is there another element like helium, neon, and argon. Between argon and krypton there are 17 elements, whereas between helium and neon, and between neon and argon there are only 7. The two kinds of

FIG. 9.—A MODIFICATION OF MENDELÉEF'S PERIODIC TABLE

SERIES	0	I	II	III	IV	V	VI	VII	VIII		
First (short)	He 4.0	Li 6.9	Be 9.0	B 10.8	C 12.0	N 14.0	O 16	F 19.0			
Second (short)	Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5			
Third (long)	A 39.9	K 39.1 Cu 63.6	Ca 40.1 Zn 65.4	Sc 45.1 Ga 69.7	Ti 48.0 Ge 72.6	V 51.0 As 75.0	Cr 52.0 Se 79.2	Mn 54.9 Br 79.9	Fe 55.8	Co 59.0	Ni 58.7
Fourth (long)	Kr 82.9	Rb 85.4 Ag 107.9	Sr 87.6 Cd 112.4	Yt 89.0 In 114.8	Zr 91.0 Sn 118.7	Cb 93.1 Sb 121.7	Mo 96.0 Te 127.5	..... I 126.9	Ru 101.7	Rh 102.9	Pd 106.7
Fifth (long)	Xe 130.2	Cs 132.8 Au 197.2	Ba 137.4 Hg 200.6	La 138.9 Tl 204.4	Ce 140.2 Pb 207.2	Ta 181.5 Bi 209.0	W 184.0	....	Os 190.8	Ir 193.1	Pt 195.2
Sixth (incomplete)	Rn 222.0	.....	Ra 225.9	.....	Th 232.1	.....	U 238.2				

ATOMIC WEIGHTS ARE GIVEN TO THE FIRST PLACE OF DECIMALS ONLY.

series were therefore named the **short** and the **long** series. These ideas might have been incorporated into a table by putting all of the elements between argon and krypton into a single horizontal row. To this there are several objections. Titanium, vanadium, chromium and manganese, although in most respects quite different from silicon, phosphorus, sulfur and chlorine, do at least exhibit respectively the same maximum positive valence numbers. Similarly, although copper is quite different from the alkali metals, it resembles them in yielding univalent positive ions; zinc is not much like the alkaline earth group metals but like them forms bivalent positive ions. By splitting the long series into two parts as shown in Fig. 9, elements which exhibit the same valence are placed in the same vertical column, and undue spreading out of the table is avoided. Each column constitutes a **group,** or family, of elements; those at the right in the columns are the **main groups** and those at the left the **subgroups.** Iron, nickel and cobalt of the first long series and the corresponding elements of the others cannot be placed according to valence or other chemical properties with any group of elements encountered in the short series. For this reason they are made to constitute an eighth group which plays the rôle of a transition group just as does the helium family. Further details of the system may be learned by studying the modified Mendeléeff table,[1] Fig. 9.

Success of the Periodic System.—In the hands of Mendeléeff and the chemists of his time, the periodic system accomplished results of such importance that its usefulness was almost immediately recognized. A few of these results may be briefly summarized:

(1) In 1869, when the periodic system was first described, several of the elements known today had not yet been discovered. Mendeléeff recognized that there must be unknown elements, and left blanks for them in his table. From the position of these blanks, he then **predicted the properties of the elements** which he believed would ultimately be found. For instance, he pointed out in 1871 that there should be an element of atomic weight

[1] Mendeléeff himself devised a number of tables to illustrate the fundamental principle of periodicity.

72 lying between gallium and arsenic. To the element he gave the provisional name ekasilicon, and predicted that its properties would place it in the fourth sub-group. He foretold in detail that it would be gray, tetravalent, and inert towards acids and alkalies; also that its chloride would be a liquid and its fluoride a solid. He went so far as to state that its density would be about 5.5, and that the chloride would have a boiling point under 100°. In 1886 germanium was discovered. Its atomic weight is 72.3, its density 5.47, it is gray, tetravalent, and rather inert towards acids or alkalies at ordinary temperatures; its chloride is a liquid boiling at 86°, and its fluoride is a solid. Two similar predictions were made and successfully verified later in the discovery of gallium and scandium in 1875 and 1879.

(2) The **method of fixing atomic weights,** based on Avogadro's law and today universally accepted, cannot be applied to elements which form either only few gaseous compounds or none at all. The use of the periodic system in this connection may be illustrated by the case of radium. One hundred thirteen grams of the element combine with 35.46 grams of chlorine. If radium is univalent, the formula of the chloride is RaCl, and the atomic weight 113. But there is no place for an element of this atomic weight in the periodic table. If, on the other hand, radium is bivalent, the formula of its chloride is $RaCl_2$. In this case the atomic weight would be 226. At the time radium was discovered, there was a vacant space for an element of this atomic weight in the alkaline earth group, and radium, with properties very similar to those of barium, fits exactly.

(3) **Corrections of data** concerning the properties of the elements and their compounds have been suggested by the periodic system. For example, the old atomic weights of some of the platinum group metals did not conform to the place in the periodic system assigned to those elements by virtue of their chemical properties. Redetermination of the atomic weights proved that the original values were incorrect.

(4) The periodic system has often been of **aid in research.** Thus the solubility of the hydroxides of the elements in the alkaline earth group increases with ascending atomic weight. This suggested that radium hydroxide might be more soluble than

barium hydroxide, and led to a new method of separating the two elements. Haber, in his search for a catalyst to be used in the synthesis of ammonia, made use of the periodic system by noting the groups in which the best of the common catalysts lay, and by then trying all of the neighboring elements.

(5) **The system is very helpful in unifying and correlating the many facts of chemistry.** Such correlation is not only one of the fundamental functions of science, but is extremely serviceable to students since it makes the facts much easier to remember. The elements still to be taken up will nearly all be presented as members of the groups to which they belong rather than as individuals, so that constant use will be made of the periodic system.

Although the foregoing illustrates the outstanding applications of the periodic system, its importance is far greater than its great usefulness indicates. In recent years it has been the stepping stone from which scientists have attempted to explore the innermost structure of the atoms. The direction in which science has developed under its guidance and the discoveries resulting from the finding of radium, will be described in the two following chapters.

Modifications of the Periodic Table.—Mendeléeff himself devised a number of different arrangements of the elements to illustrate the periodicity of their properties, and a great number of modified arrangements have been suggested since his time. Some of these are advantageous in bringing out one particular point of view, while others may be more useful for slightly different purposes. None of them affects profoundly the fundamental principle, and it is unnecessary to take them up in detail. The original Mendeléeff tables have, however, one defect from the point of view of the beginner. They do not bring out clearly the difference between the main and the sub-groups. In this respect a table devised by Harkins has considerable advantages, and will therefore be used in the subsequent discussions.

The Harkins Model.—The Harkins table is arranged in the form of two concentric cylinders. The first two series of elements are placed on a descending helix around the upper part of the outer cylinder as shown in Fig. 10. The elements on each of the

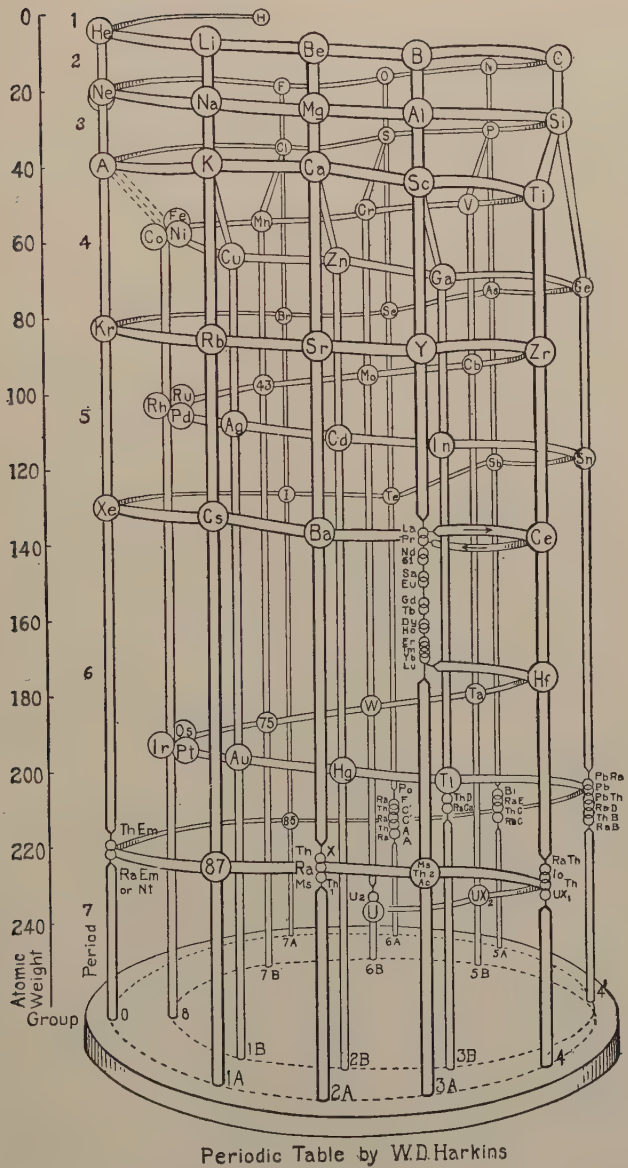


FIG. 10.

vertical lines constitute a group. The helix on the outer cylinder continues until titanium is reached, and then turns inward to the inner cylinder. It continues on this until germanium is reached, and at this point returns to the outer cylinder. The elements on the vertical lines in the inner portion of the model represent the sub-groups. In this way the relationship of the groups is made quite clear. In some instances, notably magnesium, the placing of an element in main group or sub-group is different from that of the original Mendeléeff arrangement, but on the whole the two correspond quite well.

There are some other advantages of the Harkins arrangement but these need not be taken up. Two points should, however, be noted. In the Harkins table the fourth group divides into two, beginning with titanium. Neither of the divisions is definitely a sub-group as one of them represents the beginning and the other the end of each inner series. In the second place, the peculiarity of the iron group is brought out by placing three elements together at each point where the inner helix crosses the vertical column of the helium sub-group. All the main groups are located on the outer cylinder, and are designated at the bottom of each vertical line by numerals from 0 to 7A; all the sub-groups are on the inner cylinder, and are designated by numbers from 1B to 8B. The eighth group of the inner series corresponds to the 0 group of the outer. The terms "outer" and "inner" will be found very convenient in the discussions.[1]

Characteristics of Outer Series and Groups.—The number of elements thus far discussed is too small to be the basis for a complete characterization of the regularities of the periodic system. Further verification and illustration of the points noted below will be found in the remaining chapters of the text. The student will find these generalizations well worth learning as they greatly simplify the study of the remaining material. Critical examination of each of the groups from the point of view herein presented, is the best exercise that can be devised for developing a scientific method of thought.

[1] A detachable reprint of the Harkins Table will be found in the back of the book.

Characteristics of the outer series.

(1) With increasing atomic weight in an outer series (i.e., around the outer helix in counter-clockwise direction) the **maximum positive valence or valence number increases in steps of 1 from 0 to 7.** At the fourth group the **valence 4−** appears, and the **negative valence decreases to 1−** in steps of 1 to group 7. Attention is called to the fact that the statements refer to the maximum positive valence numbers, and that elements may have valence numbers less than the maximum. Thus sulfur has the valence number 4+ in addition to the maximum 6+, and nitrogen has many valence numbers.

(2) With increasing atomic weight in an outer series, **the elements become less and less electropositive.** Beginning at the fourth group, the **electronegative character begins to appear, and increases,** reaching its maximum in the seventh group. It is essential to understand clearly what is meant by electropositive and electronegative character. An element is very electropositive if its atoms readily lose electrons and become positive ions. The number of electrons lost by a single atom is not a measure of its positive character. Thus sodium, which loses only 1 electron, is more strongly electropositive than magnesium, which loses 2 electrons, because the sodium loses its 1 electron more readily than the magnesium loses the 2. In general, the more electrons an atom must lose to go over into its ion, the less readily does this occur, possibly because of the greater difference in charge between the more highly charged ions and free electrons. In the same way, an element is electronegative if its atoms take on electrons to become negative ions. Here also, the more electrons an atom must gain to go over to the negative ion, the less readily does it do so. Thus chlorine is more negative than sulfur. Finally, an element may have a positive valence number in some compounds even if it is essentially an electronegative element. Chlorine in chlorates has the valence number 7+, and sulfur in sulfates 6+. But, in general, the more electronegative the element is, the less stable are the compounds in which it has a positive valence number. Occasional exceptions will be encountered.

(3) Although (1) and (2) are the most fundamental character-

istics, there are several properties related to (2) which should be mentioned at the present time.

(*a*) A metal is an element consisting of atoms which very readily lose electrons.[1] In the outer series **metallic character becomes less pronounced** with ascending atomic weight, i.e., with decrease in the positive character of the elements. Thus sodium, magnesium, and aluminium are the most electropositive elements of the second outer series and are metals, while the remaining less positive and the negative elements of the series are non-metals.

(*b*) With ascending atomic weight in an outer series, the elements **become less active reducing agents.** This statement follows logically from (2) since reducing agents are substances which give up electrons readily. Sodium is a powerful reducing agent, liberating hydrogen from cold water; magnesium acts on water at 100°, and aluminium acts appreciably only at higher temperatures. The remaining elements of this series are weak reducing agents. On the other hand, chlorine is a powerful oxidizing agent, because it readily takes on electrons. The **oxidizing power decreases with decreasing atomic weight** in the series.

(*c*) With increasing atomic weight in an outer series, the hydroxides [2] become less basic and more acidic. Sodium hydroxide is a strong base, magnesium hydroxide almost as strong;

[1] For a further discussion of this statement, see Chapter XXXI, page 459.

[2] The term hydroxide is here used in its broader sense (see page 86). The oxygen acids of the elements may be formulated as hydroxides. For sulfuric acid, $SO_2(OH)_2$ may be written, for nitric acid, $NO_2(OH)$, for carbonic acid, $CO(OH)_2$, etc., instead of the usual formulae, even though their more common reactions do not indicate ionization into hydroxide ions. There are several theoretical reasons for so doing; for example, to indicate that the hydrogens are probably attached to the oxygen in the compound. For our purpose the chief advantage in the formulation is to have a name which will include bases and oxygen acids. In the case of substances like aluminium hydroxide, $Al(OH)_3$, which ionizes not only into $Al^{+++} + 3OH^-$, but into $AlO_3^{---} + 3H^+$ as well, a single name is of particular advantage. The student should become accustomed to the idea of distinguishing sharply between the name, hydroxide (which may be used either for substances that ionize into hydrogen ions or for those which ionize into hydroxide ions), and the name, base (which refers exclusively to the latter class).

aluminium hydroxide is a weak base, and also a very weak acid; silicon hydroxide, $Si(OH)_4$ or H_2SiO_3, is an exceedingly weak base and a very weak acid; phosphoric acid a moderately strong acid, sulfuric acid a strong acid, and chloric acid or perchloric acid very strong acids. Although there is no simple reason why strength of the hydroxide as a base should be related to electropositive character, it is an experimental fact that the hydroxides of **strongly electropositive elements almost always are strong bases** and that the hydroxides (oxygen acids) of **strongly electronegative elements are strongly acid.** There are exceptions to this rule—thus aluminium hydroxide is a weak base, while silver hydroxide is a moderately strong one, but the rule holds in the majority of cases and is well worth remembering.

Characteristics of Outer Groups.—The preceding discussion referred entirely to changes in properties with change in position around the outer helix; it is also important to have a general idea of how the properties change along the vertical lines on the outer cylinder, i.e., within the groups. Since only one group has thus far been taken up in detail, the present discussion must be made very general, and the student may expect to become more familiar with these characteristics as other groups are taken up in the later chapters of the text.

(1) **The valence in the outer groups is quite constant.** Thus all of the elements of the first group are 1+, all those of the second group 2+, all those of the third group 3+.[1] In groups like the fifth in which the elements may exhibit several valence numbers, all of them exhibit the same valence numbers with minor differences only. However, in a group in which the elements have several valence numbers, those of higher atomic weight tend to exhibit the intermediate valence numbers. Thus phosphorus may be 3−, 3+ or 5+, and the same is true of arsenic and antimony. But although the most stable phosphorus compounds are those in which the valence number is 5+, arsenic and especially antimony are more often 3+, and bismuth forms very few compounds in which it has any other valence than 3+.

(2) With increasing atomic weight in an outer group, the

[1] There is some uncertainty about the valence of boron in its hydrides and complex ions.

elements become more electropositive. Thus fluorine forms no oxygen compounds, iodine a very stable one. Nitrogen is a non-metal; but antimony and bismuth are metals and, unlike nitrogen, form free simple positive ions.

(3) With increasing atomic weight in the outer groups, the **hydroxides become stronger bases and weaker acids.** Thus bismuth hydroxide is the only hydroxide of its group which has only basic and no acid properties, while the hydroxides of nitrogen and phosphorus are exclusively acidic. Many other illustrations will be encountered.

(4) In the preceding discussions, the second element of each group was most frequently chosen to illustrate the properties of the group. This was done because **the first member of a group usually is quite different from the remaining elements of the group except in valence.** In the first three groups, the first member of each is very similar to the elements of the next group, except in valence. Thus lithium is in many ways more like barium than like sodium; beryllium is like aluminium; and boron is extremely closely related in properties to silicon, but is not at all like aluminium.

Periodicity in Physical Properties.—In Figs. 11 and 12 are shown the changes in the melting points and in atomic volume, i.e., the volume in c.c. occupied by 1 gram atomic weight of each element. The repetition of the peaks and depressions in the curves and the recurrence of elements of the same group in the same relative position on the curves are excellent illustrations of the periodicity in properties. Dotted lines indicate portions of the curve for which accurate data are lacking. Other properties, such as magnetic susceptibility, plotted in a similar way would give similar curves.

In the melting point curve, the inactive gases occupy the minima, and the elements of the fourth group the maxima. In a few cases the melting points are so high that they could not be included without reducing the scale of the curve too greatly. Irregularities in the curve may be ascribed to the fact that many of the elements exist in more than one modification, each having a different melting point. For example, had the melting point of violet phosphorus (600°) been used instead of that of the white

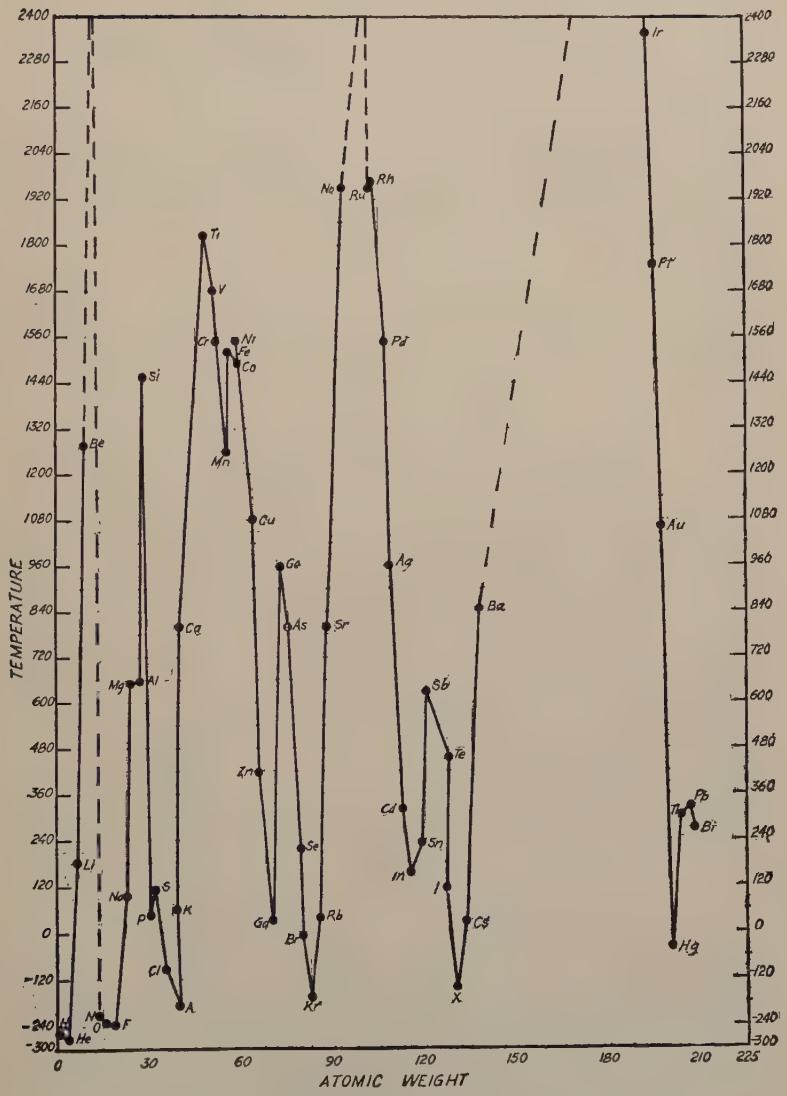


FIG. 11.—THE MELTING POINTS OF THE ELEMENTS.

variety, phosphorus would have fallen smoothly on the curve. The break in the curve between aluminium and magnesium may be due to a similar cause, although no experimental data to prove this assumption are available.

In the atomic volume curve, the inert gases would unquestionably occupy the peaks if the values were known, but very few measurements of these elements in the solid condition have

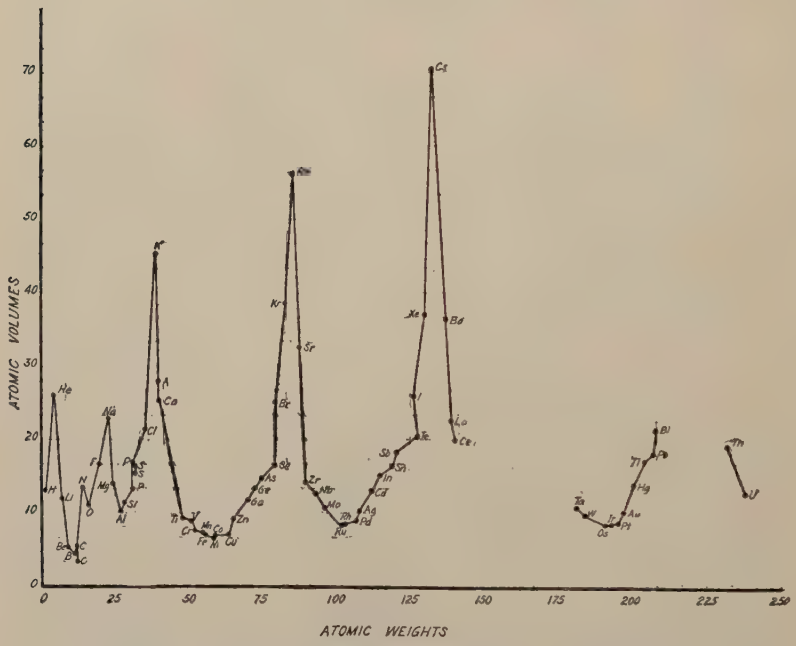


Fig. 12.—The Atomic Volumes of the Elements.

been made. The fourth group elements occupy the minima. In the melting point curve, the eighth group triads occupy little peaks, and in the atomic volume curve separate minima. Irregularities in the atomic volume and melting point curves are probably due to the same cause; moreover, the atomic volume data do not all refer to the same temperature as they should.

Characteristics of the Inner Groups and Series.—Since no elements belonging to the inner series have as yet been described,

discussion of this section of the table is deferred until the copper and the zinc groups are taken up in Chapters XXXIV and XXXV. It may be mentioned that in many respects the changes in the inner groups are just the reverse of those observed in the outer groups. In the copper group, for instance, the elements become less electropositive with ascending atomic weight, they become less active reducing agents, and their hydroxides become less basic. The valence in the inner groups is not so constant as in the outer groups. It is interesting to note also that the zinc group as a whole is more positive than the copper group, whereas in the corresponding positions of the outer series the alkaline earth group is less positive than the alkali metal group. Finally nearly all of the elements which form complex ions are in the inner groups.

Elements which do not Fit into the Periodic System.—A few elements do not fit into the system. In order to place argon with the other inactive gases, it must precede potassium although the latter has the smaller atomic weight. Tellurium is an element much like sulfur, and to fit into the sixth group must be placed before iodine, although its atomic weight indicates a position after that of iodine. Nickel and cobalt fit better as shown in the table than if the order of the atomic weights were followed. A group of elements, called the rare earths, does not fit at all into any system yet devised.

The Significance of the Periodic System.—Aside from any question concerning its usefulness, the periodic system is of great importance because its regularities imply some fundamental relationship between the elements. It brings up a number of questions the answers to which require deep insight into the structure of matter. In the following two chapters the progress made in explaining this periodicity will be described briefly. The same description will show also how it is possible to account for the facts that a few elements do not fit into the system, and that an unexpectedly large number of elements have atomic weights which are nearly whole numbers.

EXERCISES

(1) State the periodic law and make its meaning clear by an illustration.

(2) Explain why the periodic tables are divided into short and long series, and into main and sub-groups.

(3) Give several illustrations of the usefulness of periodic tables.

(4) Give the changes in chemical properties which accompany increase in atomic weight of the elements in an outer series.

(5) Answer as in (4) for an outer group.

(6) To what fundamental change in the properties of the atoms may most of the changes mentioned in (4) and (5) be ascribed? Explain.

(7) Using the regularities of the periodic system as a basis, how should rubidium differ from potassium?

(8) Answer as in (7) for oxygen and fluorine.

(9) By means of the halogen group, illustrate the statement that the first member of a group is often quite different from the others.

(10) Use the halogen group to illustrate the changes in properties which occur with increasing atomic weight within an outer group.

REFERENCES

Several of the references given in Chapters XXIII and XXIV contain discussions of the meaning of the periodic system. The following references deal with its details.

A. W. Stewart—Some Physico-chemical Themes. Chapters XVIII and XIX describe the development and applications of the periodic system, as well as numerous types of periodic tables.

A. E. Garrett—The Periodic Law (1909). A detailed book on the history and applications of the periodic system.

T. M. Lowry—Inorganic Chemistry (1922). Chapter XXXI is a short, modern presentation.

CHAPTER XXIII

RADIOACTIVITY

Toward the close of the nineteenth century interest in the periodic system, which was extraordinarily keen for a few years after it was announced, seemed to flag. To some scientists the regularities which it emphasized appeared so limited in scope, the number of exceptions seemed so large, and the failure to account for the properties of elements like the rare earths so serious, that they began to doubt that the system had the fundamental significance originally ascribed to it. At the same time their interest was drawn elsewhere by the rapid development of the chemistry of carbon compounds, by the discovery of ionization in solutions, and by the application of certain physical principles (thermodynamics) to chemistry. The beginning of the twentieth century again saw a revival of interest in the periodic system, brought about by the study of the phenomena attending the discharge of electricity through gases, and by the discovery of radioactive substances. These investigations and discoveries, interpreted with reference to the periodic system, have revolutionized the earlier views about the nature of matter.

The Discharge of Electricity through Gases.—Gases under ordinary conditions are very poor conductors of electricity. In order to pass a spark between two electrodes situated at opposite ends of a tube 20 to 30 centimeters long and filled with air at atmospheric pressure, an enormous voltage must be applied. If sparks do pass, they occur at irregular intervals and travel through the tube in zig-zag paths. But if the gas pressure in the tube is reduced, the discharge of electricity is greatly facilitated, and its nature completely changed. The irregular sparks are replaced by luminous streamers which extend from one electrode to the other, and the whole tube appears to glow with a greenish

light. With continued evacuation the streamers are broken up into very regular zones of light and darkness, and different parts of the tube display various colors. Finally, when the pressure in the tube becomes very low, resistance to the passage of the charge again increases.

These phenomena suggest that the electricity is carried through the tubes by material particles. When the gas pressure is large, these particles encounter so many of the gas molecules that it is difficult for them to pass, and those which do so must travel in zig-zag paths similar to those of gas molecules at high pressures. As the pressure decreases, the number of interfering molecules becomes less, and the passage is easier. But when the tube is almost completely evacuated, the number of particles is so small that too few to carry a current are available. The material character of the carriers of electricity is further borne out by the fact (already noted on page 42) that a piece of metal inserted in the path of the current becomes heated to redness, apparently by the impact of the particles. It has already been shown that some of these particles are electrons, produced from the gas in the tube, and that the electrons are all of the same character irrespective of the nature of the gas. But the atoms which have lost the electrons must be positively charged. The tube therefore also contains some heavier, positive particles, which move toward the negative pole and thus contribute to the passage of the current.

X-rays.—In such discharge tubes under certain conditions of pressure, the glass opposite the negative electrode becomes brilliantly fluorescent, and a new kind of radiation, called Roentgen or X-rays, is observed outside the tube. The new rays, discovered by Roentgen in 1895, are extraordinarily penetrating. They pass through substances opaque to ordinary light, and are very active in inducing chemical changes. As a result they are extensively used in medicine, both as curative agents and to photograph portions of the body hidden from the eye.

X-rays are produced whenever high velocity electrons strike a solid. Since it is difficult to maintain the necessary speed in the presence of large numbers of gas molecules, the X-rays usually originate in a vacuum tube. They are waves analogous to light waves, but of extremely small wave lengths. The waves

utilized for broadcasting in wireless telephony average about 400,000 centimeters in length; the wave lengths of light in the visible region of the spectrum vary from about 0.00007 to 0.00004 centimeters; the wave lengths of X-rays are from $\frac{1}{1,000}$ to $\frac{1}{10,000}$ as long as the visible waves. Within these limits, the various elements under the influence of bombardment by electrons of sufficiently high velocity, produce characteristic X-ray spectra, somewhat as in glowing vapors they produce characteristic spectra in the visible region of the spectrum. The X-ray spectra of the elements are independent of the nature of the compound used to produce the spectrum, while this is not always true of the ordinary spectra.

The Discovery of Radium.—The fluorescence associated with discharge tubes giving off X-rays and observed when these rays fall upon certain substances, led a French physicist, Becquerel, to investigate fluorescent substances in general in order to find out whether they also give rise to X-rays. His experiments showed that certain uranium salts affected a photographic plate just like X-rays even though the salts and the plate were separated by substances opaque to ordinary light. It was rather fortunate for the rapid development of science that Becquerel happened to possess a particularly pure sample of uranium, for most fluorescent substances do not behave like uranium in this respect. Had he carried out his experiments with some of the others, the remarkable discoveries which followed his experiments with uranium compounds might have been delayed. In conjunction with the work of Becquerel, Professor and Madame Curie undertook to examine as many fluorescent substances as possible. They found that all pure compounds of uranium give out the penetrating rays, and that in these compounds the intensity of the radiation is proportional to their uranium content. But they also discovered that certain ores containing relatively little uranium, send out much more intense radiation than do the purest uranium compounds. The only possible interpretation of this phenomenon is that these very active substances must contain a hitherto unknown element to which their great activity may be ascribed.

In order to demonstrate the correctness of this hypothesis,

Madame Curie undertook to separate pitchblende, which was the most active of the substances studied, into its components. After a long series of experiments, in which she displayed the utmost patience and skill, she finally succeeded in isolating a new element, radium. This is actually about one million times as active as uranium. The difficulties she encountered may be imagined by remembering that the pitchblende with which she worked probably contained less than 0.1 gram of radium in a ton of the ore. After a few years, the mineral carnotite replaced pitchblende as a source of radium but, even though richer in radium than pitchblende, it yielded only about 0.2 gram of the element per ton of the raw material. Recently an ore said to be the richest known has been discovered in the Belgian Congo. In spite of this, the cost of the radium is still in the neighborhood of $75,000 a gram.

Radioactivity.—The chemical properties of radium are so much like those of the metals of the alkaline earth group, especially barium, that they need not be discussed in detail. Interest in radium centers in the properties it possesses in common with some other "radioactive" elements [1] which have been discovered within the past twenty years. It has already been mentioned that these elements give off three kinds of rays, the alpha, the beta and the gamma rays. The alpha rays are generally considered, on the basis of fairly conclusive evidence, to consist of helium atoms carrying two positive charges each;[2] the beta rays consist of very rapidly moving electrons; and the gamma rays are X-rays of very short wave length. In general, a given radioactive element gives off only alpha or beta rays, but not both.

An actual **transformation of the radioactive elements** into new elements is associated with the radiation of the alpha and the beta rays. The rates of these transformations vary enormously from element to element, but are independent of the temperature. The time required to decompose one half of any given amount of radium, the half-decay period,[3] is about 1700 years,

[1] See page 5, for a definition of this term.

[2] These charged helium particles undoubtedly are helium nuclei. (See page 357.)

[3] The significance of the term "half decay period" may perhaps be made

while for other radioactive elements it is only a few minutes, and for still others millions of years, as shown in the table below. Even though the decomposition of radium is slow, there would no longer be any of it left on the earth if it were not continuously formed by the radioactive decomposition of uranium. Uranium is still present because its rate of decomposition is extraordinarily slow.

Radioactivity and the Periodic System.—The chemical properties of the element formed by any radioactive decomposition are related to those of the parent substance in a definite way, depending upon the type of ray associated with the decomposition. Radium emits alpha rays and is transformed into the gaseous element originally called radium emanation and now called radon.[1] Radium is a member of the alkaline earth group, while radon belongs to the group of inactive gases. The change represents a shift of two positions to the left (more accurately, in clockwise direction) on the outer helix of the Harkins table. Radon is also radioactive, giving off another alpha particle and going over to radium A, an element of the sulfur group. This change again represents a shift of two toward the left in the periodic table. Radium A loses an alpha particle, giving radium B which belongs, with lead, to the fourth group. Once more the loss of an alpha particle is associated with a shift of two places to the left. Radium B also is unstable, but it gives off beta rays, that is, it loses an electron in its decomposition. Here the shift in position is in the opposite direction, for the product, radium C, fits into the fifth group.[2] The complete series of

clearer by the following considerations. The fraction of any quantity of a given radioactive element which decomposes in a given time is a constant quantity. Thus, of 1 gram of radium, one-half decomposes in 1700 years. During the next 1700 years one-half of the remainder decomposes, leaving $\frac{1}{4}$ of a gram. The next 1700 years bring about decomposition of one-half of the last named amount, so that $\frac{1}{8}$ of a gram is left, and so on. Evidently complete decomposition would require infinite time. Consequently only the time necessary for the decomposition of a definite fraction (for example, one-half), can be stated.

[1] The name niton was used at one time.

[2] Some of the substances mentioned are so little known that their position in the periodic system is purely hypothetical. But the relationship illustrated

changes which uranium and its decomposition products undergo is shown in Table XVII. The names of the elements are indicated by their symbols; the nature of the decomposition is shown by an alpha or a beta placed above the arrow, and the number of the group of each element by a Roman numeral above the symbol.[1] Below each symbol is the approximate atomic weight of the element and below that, the approximate half-decay period. " y " means years, " d " days and " m " minutes.

TABLE XVII

THE URANIUM SERIES OF RADIOACTIVE SUBSTANCES

VI		IV		V		VI		IV	
U	$\xrightarrow{\alpha}$	UX_1	$\xrightarrow{\beta}$	UX_2	$\xrightarrow{\beta}$	U_2	$\xrightarrow{\alpha}$	Io (nium)	$\xrightarrow{\alpha}$
238		234		234		234		230	
5×10^9 y.		23 d.		1.2 m.		(2×10^6) y.		(7×10^4) y.	
II		O		VI		IV		V	
Ra.	$\xrightarrow{\alpha}$	Radon	$\xrightarrow{\alpha}$	Ra. A	$\xrightarrow{\alpha}$	Ra. B	$\xrightarrow{\beta}$	Ra. C	$\xrightarrow{\beta}$
226		222		218		214		214	
1700 y.		3.8 d.		3 m.		27 m.		20 m.	
VI		IV		V		VI		IV	
Ra. C_1	$\xrightarrow{\alpha}$	Ra. D	$\xrightarrow{\beta}$	Ra. E	$\xrightarrow{\beta}$	Ra. F	$\xrightarrow{\alpha}$	Ra. G (Radio-lead)	
214		210		210		210		206	
2 m.		16 y.		4.8 d.		136 d.		end	

In addition to the points already discussed, the table brings out a number of others which should be noted, as they will be taken up in more detail in the following chapter. In the first place every alpha change is accompanied by a loss of 4 units in atomic weight, since the alpha particle lost is a charged helium atom with an atomic weight of 4; a beta change causes no measurable change in atomic weight, since the loss of weight due to the escape of 1 electron is too small to be determined experimentally. As a result of the beta changes, elements of different properties but identical atomic weight are formed. The second point to be noted is that the formation of radioactive elements

is so well established by authentic instances that the whole series of transformations may be used as a simple illustration.

[1] No distinction between main and sub-groups is made.

finally ceases, for radium G is apparently stable. Very convincing, though indirect, evidence has led to the theory that it is identical in its reactions with ordinary lead.[1]

X-ray Spectra of the Elements.—The alpha and the beta particles lost by the elements in radioactive transformations are believed to come from the nuclei of the atoms. An alpha change therefore means a loss by the nucleus of two positive charges; a beta change a gain of one in the net positive charge, since losing one negative charge is equivalent to gaining a positive one. This idea applied to the shift of position in the periodic system accompanying an alpha or a beta change leads at once to the conclusion that **the nucleus of any element contains one more positive charge than does the nucleus of the preceding element.** This conclusion has been verified in a striking way by the X-ray spectra of the elements.

Just as white light may be resolved by suitable apparatus into light of various wave lengths, so X-rays may be resolved and analyzed. Each element emits a characteristic type of X-rays, as has already been mentioned, and when the elements are arranged in the order of the wave lengths of their characteristic spectra, whole numbers may be assigned to each element.

These numbers vary inversely with the square root of the wave length of the spectral lines, and have been shown to represent the number of positive charges on the nucleus of the atoms. The numbers are found to correspond exactly to the position number of the element in the periodic system; for example, aluminium is the thirteenth element in the periodic system (considering hydrogen to be the first) and the number obtained from the X-ray spectrum is 13.[2]

Atomic Numbers and Atomic Weights.—When the position numbers of the elements, more commonly called the **atomic**

[1] There are two radioactive series beside that described here. The actinium series is probably a branch of the uranium series. The thorium series, as its name indicates, starts with thorium and ends with thorio-lead. The second member is meso-thorium, which may be used in place of radium for luminous watch dials. Thorium emanation resembles radon and the radium and thorium series are in many other respects quite similar.

[2] The X-ray spectra of the lighter elements and of the inactive gases have not yet been obtained, but are assumed to fit with the rest.

numbers,[1] are determined by the X-ray method and are used in arranging the elements in the periodic system, all elements fall into places which are in accord with their chemical properties. In the original periodic tables based on atomic weights, it was necessary to place several elements in inverted order to fit them into their proper groups. The atomic numbers are thus in a certain sense more fundamental properties of the elements than the atomic weights. Furthermore they gave the first experimental proof that the periodic table possesses the fundamental significance it was always suspected of having. For the atomic numbers represent positive charges on the nuclei of the atoms, and therefore numbers of electrons surrounding the nucleus. The relationship between chemical properties and atomic numbers therefore means a definite relationship between chemical properties and the structure of the atoms.

Further evidence on this point is found in the displacement series of radioactive substances. Loss of an alpha particle from the nucleus means a loss of two positive charges and therefore a decrease of two in the atomic number. But this change has been shown by experiment to be accompanied by a displacement of two positions to the left in the periodic system and by the change in chemical properties corresponding to such a shift. This again means that chemical properties must be closely related to the positive charge of the nucleus. To what sort of hypotheses these results have led, will be described in the next chapter.

The great significance of the atomic numbers has led some writers to make the statement that too much emphasis has been laid in the past on atomic weights. Although this may be true from certain points of view, the statement is certainly very misleading. Atomic weights are the basis of all calculations dealing with equivalent quantities of reacting substances. They can never lose their practical importance.

The method of measuring the wave lengths of X-rays is most interesting. Ordinary light may be resolved by means of a grating. The principle on which gratings operate is most easily understood by considering a piece of glass on which opaque lines are drawn at exactly

[1] For a list of the atomic numbers of the elements see the table on the inside back cover of the book.

equal intervals. The light passes through the clear spaces, and each of these thus becomes the origin of a train of light waves. As these spread out, they interfere with each other. Where crest meets crest, the waves reinforce, but where trough meets crest they extinguish each other. Examined through suitable apparatus, light of a single wave length issuing from such a grating appears as a series of dark and of light lines. The positions of reinforcement and of extinction are determined by the wave length of the light. Consequently, if the light is ordinary white light, the various colors will be extinguished in different parts of the field and a spectrum will be seen.

In order that a grating may operate correctly, the spacing of the lines must be exactly even, and the number of lines must bear a certain relation to the wave length of the light. The shorter the wave length, the greater is the number of lines required. To resolve ordinary light, sufficiently for accurate measurement, from 50,000 to 100,000 lines per inch are required. It is impossible to make such a grating of glass, but it has been possible to make gratings containing this enormous number of lines, accurately spaced, by ruling the lines on metal mirrors.

The number of lines on a grating for analyzing X-rays would have to be considerably greater than needed for ordinary light, because the wave lengths of X-rays are much smaller. Ruling a grating is therefore out of the question. It occurred to a German physicist, v. Laue, that crystals consist of material particles (atoms or molecules) of minute size arranged in definite order. The regular alternation of material particle and empty space might thus act like the lines and spaces of a grating. Actual experiment corroborated the hypothesis.[1]

The amount of dispersion produced by a diffraction grating depends not only on the wave length of the incident light but also on the distance between the lines of the grating. From the character of the interference pattern obtained with light of known wave lengths, the spacing of the lines may therefore be calculated. In the same way, from the interference patterns obtained by the use of crystals and X-rays, the nature and arrangement of the material points which constitute **crystal structures** have been determined.

Crystal Structure.—Crystals consist of matter arranged in the form of more or less regular geometrical figures bounded by planes. Early

[1] The interference patterns obtained by using crystals in the study of the wave lengths of X-rays are more complex than those obtained by a ruled diffraction grating and ordinary light. In the crystal the material particles do not all lie in a single plane, and reflection and diffraction occur at every plane in which the particles lie.

investigators concerned themselves largely with the outward appearance of the crystals, with classifications into groups of the various types observed, and with the relationship between crystalline form and chemical composition. The first important result of this work was the discovery that there are very definite types of crystals which can be classified into a relatively small number of groups based on their symmetry. In the second place it was found that each substance always forms the same sort of crystals within a definite temperature range. Even though the appearance, or shape, of the crystals may not always be the same, their form as determined by the interfacial angles and other geometric properties is constant. A few of the crystal groups thus discovered are so often used in describing the appearance of substances, that several of them are illustrated in the following drawings (Fig. 13).

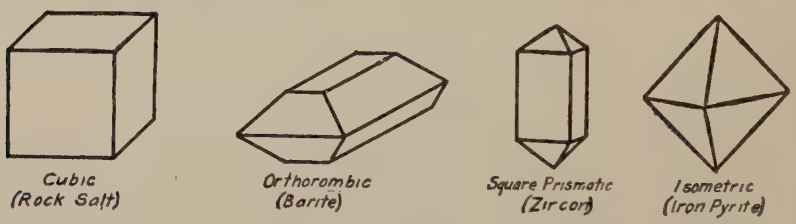


FIG. 13.

The rise of the molecular and atomic theories, however, shifted the emphasis to the study of the meaning of these crystal forms. The first step in this direction was the development of a purely geometrical theory of crystal structure somewhat in the following way. Crystals were imagined to consist of small units of pattern, called crystallographic units. The units were thought of as bounded portions of space all of which have the same volume and the same shape. For example, the units may be supposed to be equal spheres, each with a spot on its surface, although any other figure and any other method of indicating its orientation might be chosen. The geometrical problem then is to determine the number of different arrangements in space according to which each sphere is surrounded by the same number of spheres, and has about it the same configuration of spots as any other one of the spheres. If, for instance, the spheres should be thrown at random into a basket and the resulting accidental arrangement of spots around any one sphere studied, the pattern found would unquestionably be different from that of the spots around some other sphere. But the arrangement of spheres can be altered according to some plan which will make the pattern about all

of the spheres identical. This identity is essential if the patterns are to be made the basis of structures which, like actual crystals, have the same geometric properties whether they are large or small.

The geometrical study thus roughly outlined showed that there are 230 possible arrangements of crystallographic units meeting all of these requirements. These 230 arrangements can be divided into 32 classes and 7 systems of symmetry. Furthermore, the patterns obtained as a result of these studies possess all of the geometrical properties observed in actual crystals. But, although from this geometrical theory of crystals the external properties of a crystal can be calculated by assuming it be built of one of the 230 patterns, the reverse deduction cannot be made; that is, the internal structure to which a given crystal conforms

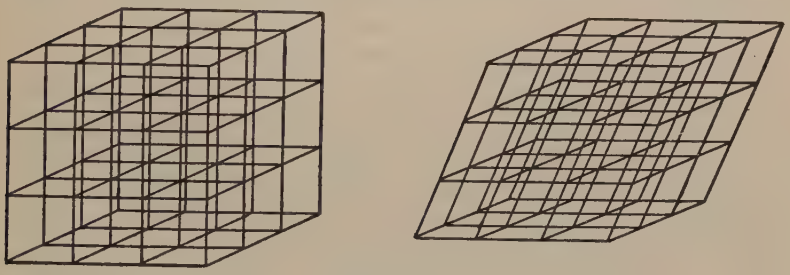


FIG. 14.—TYPES OF SPACE LATTICES.

cannot be determined from measurements of the interfacial angles and axes of the crystal. Not until the rise of the X-ray analysis of crystals did the solution of this problem seem even remotely possible.

A further simplification in the study of crystal structures is brought about by supposing that in these patterns the space is partitioned into little cells by three series of parallel planes drawn through the similar points, that is, in the illustration of the method used above, through the spots on the spheres. The 230 possible arrangements of crystallographic units can thus all be referred to 14 different configurations of the sets of parallel planes, or better, of the little parallelopipeds bounded by the planes. These configurations are called **space lattices.** (See Fig. 14.) According to modern crystallographic theory the material particles of which the crystals are built occupy the points at which three sets of planes intersect, that is, the points of the space lattices. But although the number of possible lattices is not great the number of crystal forms is relatively large, and the arrangements not always easy to visualize. Thus in some crystals, the atoms of one of the constituent elements of

the compound lie on the points of one lattice, and those of the other element on another. In such a crystal, the form taken is that of an arrangement built up by the interpenetration of the two lattices. Because of these possible complexities the matter is not carried farther here; for those interested, references dealing with it are given at the end of the chapter.

Modern investigations with the X-ray method have shown that the crystallographic units actually represent particles of matter, and have made it possible to determine what these particles are. In some cases they have proved to be groups of molecules, in others single molecules, in still others atoms, and in salts and other strong electrolytes, ions. It has further been possible to measure the distance between the planes. In the case of sodium chloride, for example, the length of one of the elementary cubes, of which the crystals may be considered to be built, is only about one hundred millionth of an inch.

Energy Changes Accompanying Radioactive Transformations. —When radioactive elements decompose, the alpha particles or electrons are shot out from the atoms at enormous velocities. The energy required to impart this velocity to the material particles must have come from the decomposition of the atom. Atoms are thus seen to be storehouses of enormous quantities of energy. When the moving alpha particles or electrons strike other matter, their motion is stopped, and their energy transformed into heat. One gram of radium in this way produces about 120 calories per hour. The total amount of heat given out by the complete decomposition of the radium would be about 2,000,000,000 calories per gram, an equivalent of the heat produced by the burning of about 1 ton of coal. But the transformation of radium is so slow that the heat cannot be utilized effectively.

A great deal of discussion has been aroused by the facts just described. The suggestion has been made that if decomposition of the more stable elements could be initiated in some way, man would have in his control unimaginable stores of energy which might ultimately displace coal, water power and all of our present sources of energy. But thus far these ideas rest upon neither an experimental nor upon a sound theoretical basis. The common elements of the earth are stable substances in contrast to the radioactive elements, and more energy might be required to cause their decomposition than could be regained in the form of motion imparted to the products of disintegration.

The heat given out in the disintegration of the known or unknown radioactive elements may, however, have played an important rôle in the earth's history, because it may be in part responsible for the slow rate at which the earth has cooled and for some of the energy radiated by the sun. For further discussions of this phase of the matter a modern text book of geology should be consulted.

The study of radioactivity is, today, a science by itself, and in this chapter it has been possible to give merely an outline of some of its phases which have influenced chemical thought. The new ideas to which it is leading are briefly described in the next chapter.

EXERCISES

(1) In what way do X-rays differ from visible light?

(2) (*a*) What reason is there to believe that the intensity of radiation from substances containing uranium depends on the amount of uranium present? (*b*) What was the evidence for the belief that certain uranium ores contain a more active radioactive substance than uranium?

(3) What are the three kinds of rays given out by various radioactive substances?

(4) (*a*) In what way may the changes in chemical properties which occur as the result of the ejection of an alpha particle from an atom be described in terms of the atomic weights and of the periodic tables? (*b*) Answer as in (*a*) for the results of the ejection of a beta particle.

(5) What is meant by the term "atomic number"? How is the atomic number of an element determined?

REFERENCES

Soddy, F.—The Interpretation of Radium. An excellent and interesting book in non-technical language.

Russell, A. S.—An Introduction to the Chemistry of the Radioactive Substances. Deals with the chemistry of the radioactive elements and their relations to atomic numbers, periodic system and theories of atomic structure. (See also References to Chapter XXIV.)

Bragg, W. H. and W. L.—X-Rays and Crystal Structure. The difficult subject matter is treated in as simple a manner as possible. Chapters V and VI treat of the subjects touched on in this text.

Lowry—Inorganic Chemistry. Pages 207–220 discuss crystals, giving many illustrations.

CHAPTER XXIV

THE STRUCTURE OF ATOMS AND OF MOLECULES

Interpretations of Valence.—Isotopes

The subject matter thus far presented consists of the well-established facts of chemistry and of the theories which rest upon firm experimental foundations. In this chapter some of the newer ideas about the constitution of matter are to be taken up. Many of them are as yet highly speculative and await further experimental verification. It is, therefore, not surprising that divergent views should be held about most of them. Physicists, in making attempts to picture the architecture of atoms, have sought to explain the spectra of the elements, and have therefore stressed the motions of the electrons within the atoms in order to account for their ability to send out trains of light waves. The hypothesis advanced by Bohr is the most important one from this point of view. Chemists, on the other hand, have sought to find in hypotheses concerning the structure of atoms an explanation for chemical phenomena, and have emphasized the location of the electrons in the atoms. The ideas advanced by G. N. Lewis in the United States and later modified somewhat by Langmuir, and by Kossel in Germany have had the greatest success in this field. The two pictures are of course supplementary to each other, and will ultimately be combined into a more comprehensive hypothesis which embraces both; but this cannot be accomplished completely until more facts have been discovered and more theoretical work has been done.[1] Since it is impossible in this text to discuss both types

[1] Lewis has suggested that the two types of theory may be unified by the view that the electrons are rotating about fixed centers or foci, and that these centers represent the fixed positions of the electrons assumed in his hypothesis.

of hypotheses (or for that matter either of them in great detail) the view which emphasizes chemical phenomena has been chosen for presentation.

The Rutherford Atom.—All the modern hypotheses about atomic structures are based upon fundamental experiments carried out by Rutherford. In order to explain the scattering of alpha rays by matter, he assumed that the atom consists of a very small, very dense nucleus carrying a positive charge and surrounded at a relatively large distance by electrons. Practically the whole of the mass of the atom is centered in the minute nucleus. In the simple hydrogen atom the nucleus probably occupies a much smaller volume than the electron; for the case of the more complex atoms the relative dimensions are not known with much certainty. The picture thus presented recalls that of the solar system, but it must be remembered that the relative dimensions and distances in the atom are entirely different from those of the solar system, and that the atom is in most cases probably more complicated. The more recent hypotheses are developments of the Rutherford atom, in which the arrangement of the electrons surrounding the nucleus and the composition of the nucleus have been considered.

The Proton.—Hydrogen consists of the simplest atoms. They are believed to be composed of a simple nucleus around which rotates a single electron. The hydrogen nucleus must be looked upon as the unit positive charge, called the **proton,** as the electron is the unit negative charge. All other nuclei are supposed to be built up of protons and electrons. Thus the nucleus of the helium atom probably contains 4 protons held together by 2 electrons. This structure accounts for the facts that the atomic weight of helium is 4, and that it has a nuclear charge of only 2. Attention must be called to an apparent discrepancy between this hypothesis and the actual facts. The atomic weight of hydrogen is 1.008 while that of helium is exactly 4. It might be expected that if there are 4 protons in a helium nucleus, the atomic weight of the element should be 4.032. In order to account for the difference, it has been assumed (Harkins) that, in packing the 4 protons as closely as they are believed to be packed in the nucleus, a loss

in mass occurs.[1] The same loss would occur whenever protons are packed into nuclei, and on the basis of this hypothesis whole numbers would be predicted for the atomic weights of all elements. As has already been pointed out there are many more integral atomic weights than can be explained by chance alone, and the hypothesis presented accounts satisfactorily for this phenomenon; why not all elements have integral atomic weights will become clear later.[2]

The Lewis Hypothesis of Atomic Structure.—Hypotheses dealing with the arrangements of the electrons around the nucleus are based largely on the periodic system and on the properties of the inactive gases. The elements of the helium group are characterized by their inability to form compounds. The assumption logically follows that the atoms of these elements are extraordinarily stable, and have no tendency either to lose or to gain electrons. Consequently their structures must be of fundamental importance in understanding the nature of other atoms. The helium atom consists of a nucleus with a net positive charge of 2 and of 2 extra-nuclear electrons. The most symmetrical arrangement of such a group has the nucleus in the center of a line drawn between the two outer electrons (Fig. 15). Neon atom has a nuclear charge of 10+ and 10 electrons in the outer portion of the atom. Lewis assumes (for reasons which will appear from the following discussion) that 2 of the 10 electrons lie close to the nucleus, as in the helium atom, and that the remaining 8 are located in an outer zone, symmetrically disposed.

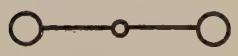


Fig. 15.

[1] The Einstein theory of relativity predicts the possibility of a relationship between mass and energy.

[2] Early in the nineteenth century Prout advanced the hypothesis that all elements were built up by the union of hydrogen atoms. The hypothesis was soon discarded because it was found that the atomic weights, when accurately determined, were not integral multiples of the atomic weight of hydrogen. The modern theory is a simple modification of Prout's, in which hydrogen nuclei are substituted for hydrogen atoms and a constant "packing effect" is assumed. Nevertheless scientists were justified at the time in not accepting Prout's hypothesis, for it did not fit the known facts, nor did it suggest experiments for finding the cause of the discrepancy.

The most symmetrical arrangement of 8 electrons is at the eight corners of an imaginary cube. This is represented in Fig. 16; in examining the drawing it must be remembered that the lines and planes are put in merely to make the perspective clear; only nucleus and electrons are realities. The argon atom consists of a nucleus with a charge of 18+ and 18 outer electrons. The arrangement is supposed to be like that of neon, except that there is a second layer of 8 electrons arranged in cubic fashion outside the first layer. The recurrence of the arrangement of electrons in groups of 8 has led to naming this hypothesis the theory of the "cubical atom" or the theory of "octets." The latter name is preferable; the atoms are not supposed to be cubical. It is, indeed, difficult to assign any shape to an assemblage of particles in rapid motion, even though these particles may, on the average, be disposed in space in a symmetrical way.[1]

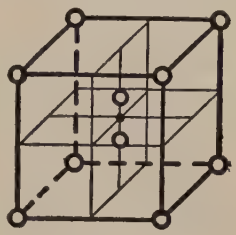


FIG. 16.

From these fundamental structures, the arrangements of other atoms and the properties of the corresponding elements are deduced on the assumption that **all atoms have a tendency to revert to one or another of the stable configurations.** Lithium atom has a nuclear charge of 3+. Of its 3 electrons, 2 are supposed to lie relatively close to the nucleus as in the helium arrangement, and the third to lie in the first outer zone. (Figure 17.) The atom may revert to a stable configuration in two ways, of which only one need be considered at present. Should the lithium atom lose the electron situated in

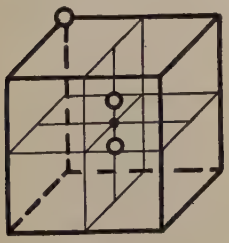


FIG. 17.

[1] Another stable arrangement of 8 electrons in the outer shell is a tetrahedron with a pair of electrons at each of the four corners. The advantage of this picture is that it illustrates the tendency of electrons to act in pairs. It also fits best the facts of stereoisomerism in carbon compounds and accounts most simply for triple bonds. (See pages 420 and 429.) For the elementary discussion of this text either picture is satisfactory, but the cubical one is more readily visualized.

the outer zone, the resulting aggregate would have the arrangement of the helium atom. But it would have one more positive charge (3+) than electrons (2), and would therefore be a positively charged particle; in other words, the univalent positive lithium ion. The great tendency of lithium to become lithium ion by loss of 1 electron is thus explained.

In similar fashion the simple properties of beryllium and of boron may be accounted for. The former has 2 electrons disposed as in helium, and 2 in the outer zone. To go over to a stable configuration, it loses the 2 outer electrons and becomes bivalent positive ion. In this case, however, the double positive charge on the ion makes it much easier for electrons to be drawn back to the charged aggregate. Beryllium is therefore less electropositive than lithium, and beryllium ion has a greater tendency to revert to beryllium atom than has lithium ion to revert to lithium atom. Boron has a nuclear charge of 5+; 2 electrons are arranged as in helium and 3 are in the outer zone. Hence boron is trivalent positive, but is less electropositive than either lithium or beryllium, because of the larger difference in charge between nucleus and the outer electrons.

The situation is somewhat different for an element like fluorine, which has a nuclear charge of 9+. There are supposed to be 2 electrons near the nucleus as in helium, and 7 in the outer cube. (Figure 18.) To go over to the helium arrangement, it would have to lose 7 electrons. The residual aggregate would have an excess positive charge of 7 units, and would therefore have an enormous tendency to recapture electrons. On the other hand, the fluorine atom could become a stable aggregate by taking on 1 electron, thus completing the first octet and assuming the neon arrangement. The most outstanding property of fluorine is its great tendency to become univalent negative fluoride ion by the gain of 1 electron. In similar fashion, oxygen atom, which has 2 electrons in the helium position and 6 in the first octet, tends to complete the octet by taking on 2 electrons. Oxygen therefore is bivalent negative, and has a considerable

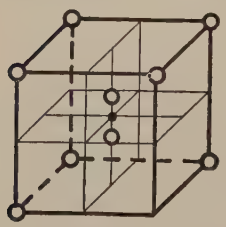


Fig. 18.

tendency to go over into oxide ion. It is not so electronegative as fluorine because of the greater difficulty of capturing and retaining the 2 extra electrons. The fact that nitrogen is trivalent negative may be explained in analogous fashion.

An extension of this line of reasoning leads to the conclusion that carbon might revert to the helium arrangement, becoming 4 positive by loss of 4 electrons, or to the neon arrangement, becoming 4 negative by the gain of 4 electrons. Carbon should have somewhat greater tendency to be electropositive than electronegative, because the helium arrangement is more stable than the neon arrangement.[1] The fact that the carbon compounds in which carbon has the valence number 4+ (for example carbon dioxide) are more stable than those in which the valence number is 4— seems to bear out this deduction. But obviously the fact that carbon never forms either simple positive or simply negative ions requires further discussion. which will be taken up later.

In the outer series of the periodic system the Lewis hypothesis thus accounts for the changes both in the numerical value and sign of the valence with increase in atomic weight. It also accounts for the facts that the elements within an outer group become more electropositive with increase in atomic weight and that the valence is constant within the group. Sodium atom has a nuclear charge of 11 and 11 electrons. Two of the latter may again be imagined to lie relatively close to the nucleus as in helium, 8 lie in the first completed octet, and the eleventh occupies a single place in the second octet. By losing this eleventh electron, sodium atom goes over to the neon arrangement, and becomes sodium ion. Since the electron lost is separated from the nucleus by a considerable distance, and is screened from it by the first octet, the outer electron is lost more readily than the outer electron of the lithium atom. Although sodium thus has the same valence as lithium, the former is the more electropositive. On the other hand chlorine, with 2 electrons in the inner zone, 8 in the first octet, and 7 in the second

[1] Helium has the lower melting and boiling point, indicating smaller attractive forces between the molecules; helium nucleus is the product of many radioactive disintegrations, while neon appears never to be so produced.

octet, may go over to the argon arrangement by gaining 1 electron and becoming chloride ion. Since the added electron is farther from the positive nucleus than in the case of the fluoride ion, it is not so firmly held, and chlorine is less electronegative than is fluorine.

The Formation of Salt-like Compounds by the Complete Transfer of Electrons.—Although lithium atoms have a great tendency to lose electrons, a mass of lithium cannot lose a great number of them permanently, unless some substance is on hand to take them up, because the attraction of the residual positive charge on the lithium would draw the electrons back again. On the other hand, fluorine, in spite of its great tendency to gain electrons, cannot take them up unless electrons are available. But if lithium and fluorine are brought into contact with each other, the electron from the lithium goes to the fluorine. An aggregate consisting of lithium ions and fluoride ions is thus formed. Unless the ions are separated by a medium of high dielectric constant, such as water, they are held together by electrostatic attraction and form molecules of lithium fluoride. All strongly electropositive and electronegative elements react with each other in similar fashion.

The Crystal Structure of Salts.—The hypothesis that salt-like substances are formed by the complete transfer of electrons from the positive to the negative element has received interesting confirmation from the study of the crystalline structure of salts by the X-ray method (see page 351). In the case of sodium chloride crystals, for example, the material particles at the corners of the cubes which constitute the structure of the crystal, are particles of sodium and of chlorine as shown in Fig. 19, and not particles of sodium chloride. Since the sodium and the chlorine are unquestionably charged, ionization, in a certain sense of the word, has occurred before the sodium chloride is dissolved.[1] In contrast to this picture is that of the crystals

[1] The fact that solid sodium chloride is a non-conductor of electricity is due in part to the fact that crystals are so rigid that the "ions" cannot flow with the current. Other factors must doubtless be taken into consideration also. In salt crystals, secondary attractive forces, such as those which cause the formation of complex ions may also be at play.

of un-ionized organic substances. In these the material particles at the corners of the geometric figures of which the crystals are constituted, appear actually to be molecules and not atoms or ions in the small number of cases thus far completely investigated.

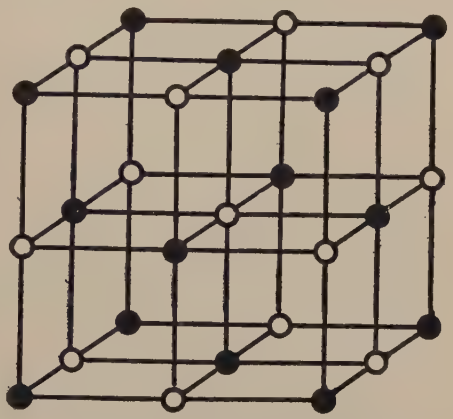


FIG. 19.—SCHEMATIC REPRESENTATION OF A CRYSTAL OF SODIUM CHLORIDE.

The shaded circles represent chloride, the unshaded ones sodium ions or atoms.

Compound Formation by Sharing of Electrons.—There are very many substances with chemical and physical properties which do not indicate the slightest trace of ionization. For these it would be illogical to assume complete transfer of electrons from one atom to another. Thus there is no reason to believe that the fluorine molecule, which is formed by the union of 2 highly electronegative atoms, contains 1 fluorine atom which has lost an electron and another one which has gained an electron. For such cases the Lewis hypothesis assumes that compound formation occurs by the **sharing of electrons.** To visualize this mechanism of compound formation, imagine two cubes placed edge to edge as shown in Fig. 20. To make the picture clear, the electrons are indicated by circles; those of the one fluorine atom are shaded and those of the other unshaded, not because there is any difference between them, but merely to show how the sharing

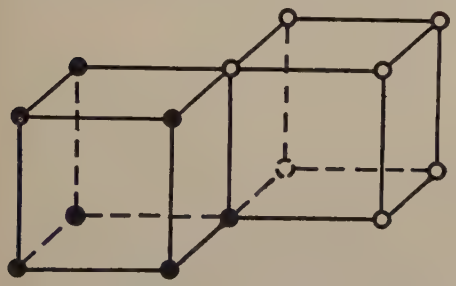


FIG. 20.—SCHEMATIC REPRESENTATION OF FLUORINE MOLECULE.

occurs. Also the cubes are drawn as if actually in contact. The reader must bear in mind that the lines are put in merely to indicate the imaginary figure, and that only the circles, which represent electrons, have any significance. Each one of the shared pair of electrons is probably displaced somewhat from its normal position, so that the pair might be said to lie **between** the 2 atoms.[1] The formation of oxygen molecules may be pictured in a similar way. Each oxygen atom has 6 electrons in the outer octet,[2] and must therefore share 2 pairs of electrons with another atom. Such a union may be visualized by imagining two cubes placed face to face as shown in Fig. 21.

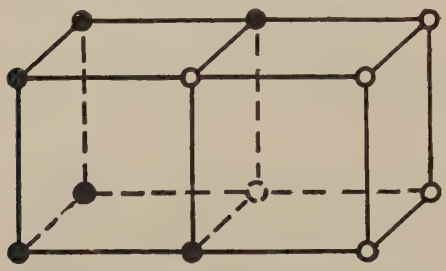


FIG. 21.—SCHEMATIC REPRESENTATION OF OXYGEN MOLECULE.

The sharing of electrons may of course also cause formation of compounds between atoms of different elements. Carbon has only 4 electrons in the outer octet. The latter may be completed by sharing electrons with 4 chlorine atoms, each of which needs to share in 1 additional electron. This is illustrated in Fig. 22.

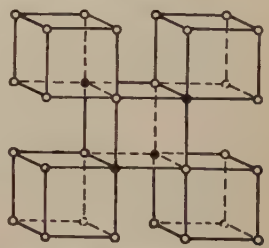


FIG. 22.—SCHEMATIC REPRESENTATION OF THE MOLECULE OF CARBON TETRACHLORIDE.

Single and Double Bonds.—According to the hypothesis just

[1] The sharing of electrons may be indicated also by writing the symbol of each atom surrounded by dots which represent the electrons in the outmost octet of each. The pair of electrons between the atoms is the shared pair. Thus fluorine molecules may be represented by the formula

$$:\ddot{\underset{\cdot\cdot}{F}}:\ddot{\underset{\cdot\cdot}{F}}:$$ and oxygen molecules by $$:\ddot{\underset{\cdot\cdot}{O}}::\ddot{\underset{\cdot\cdot}{O}}:$$

[2] The two electrons in the inner portion of the oxygen atom need not be considered as, in compound formation, only the electrons in the incompleted octet are of importance. These electrons are therefore called the "valence electrons."

described, 2 or 4 electrons may be shared by 2 atoms to complete octets and form compounds. In the former case, the elements are said to be joined by a **single bond,** and the union may be indicated very simply by drawing a line between the symbols of the elements, as in the formula for the fluorine molecule, F—F. When 2 pairs of electrons are shared, the atoms are said to be joined by a **double bond** as is indicated in the formula for molecular oxygen, O═O, or for carbon dioxide O═C═O. The distinction between the single and the double bond is by no means a hypothetical one; it was recognized long before the electron theory had been thought of, and is an expression of a distinct difference in behavior between two classes of molecules. Compounds in which all atoms are joined by **single bonds** are **saturated,** while compounds containing atoms joined by **double bonds** are **unsaturated.** (See pages 99 and 420.)[1]

Hydrogen.—The reason why hydrogen is not included in the periodic system must have become clear from the discussion of the rôle played by its nucleus in the building up of the other atoms. It is unique, and belongs to no group and to no series. The hydrogen atom loses its 1 electron fairly easily to form hydrogen ion; in this respect it resembles the alkali metals which also form univalent positive ions, but hydrogen is much less electropositive than are these metals. On the other hand, the hydrogen nucleus may attach itself to other atoms by sharing of electrons. This property is shown in many of the hydrogen compounds. The simplest of these is hydrogen molecule, in which the 2 hydrogen nuclei are bound to each other by a pair of electrons held between them. In being bound to other atoms by one pair of shared electrons, hydrogen behaves somewhat as do the halogens. That hydrogen, which is in many respects chemically similar to the electropositive alkali metals, should be so readily replaced in organic compounds by the very electronegative halogens (see page 422) was at one time considered one of the anomalies of chemistry; the simple explanation just given for this phenomenon is one of the

[1] Triple bonds, such as are supposed to occur in acetylene, HC≡≡CH, are visualized more readily by the tetrahederal arrangement mentioned in the footnote on page 359.

signal achievements of modern hypotheses of atomic and molecular structure.

The behavior of hydrogen indicates that there are two other relatively stable arrangements of nucleus and outer electrons besides those characteristic of the inactive gases. The ease with which hydrogen ions are formed, and their relatively small tendency to revert to the atomic condition must mean that the lone hydrogen nucleus is fairly stable. On the other hand, the great stability of hydrogen molecules indicates that the hydrogen nucleus associated with 2 electrons is also a stable configuration. These 2 electrons are usually paired electrons, shared with some other atom, but in a few compounds hydrogen actually constitutes the negative ion, because an extra electron is transferred to it. (See the hydrides of the alkali and of the alkaline earth group metals, pages 481 and 492.)

Polar and Non-polar Compounds.—The two mechanisms postulated by the Lewis hypothesis for compound formation suggest the existence of two different types of compounds. Those formed by **complete transfer of electrons** may be looked upon as consisting of a positive and a negative part. They are the electrolytes, and are often called **polar** compounds. Those formed by sharing electrons are not ionizable and do not contain parts to which **unit** positive or negative charges may be assigned. They are called **non-polar** compounds.

There are, however, many reasons for believing that the distinction between polar and non-polar unions is one of degree, rather than a sharply definable difference. The assumption of complete lack of polarity is inconsistent with many of the properties of non-ionized substances, a large number of which behave as if they contain positive and negative groups, although these groups are not free enough to exist as ions. Partial polarity may be explained by the assumption that the pairs of shared electrons lie closer to one of the atoms involved than to the other.[1]

[1] There is an interpretation of partial polarity which probably agrees more closely with the facts than the idea that the pair of shared electrons lies closer to one atom than to the other. It is that the pair of electrons continually vibrates between the two atoms, and that certain molecules are chemically more active when the pair approaches a particular one of the two atoms. In

The important point for the beginner is not to make a list of applications to specific cases, but to grasp the general idea that substances are classified into two great groups, and that compounds exhibiting various degrees of gradation exist between the two extremes.

It is often difficult to decide whether compounds should be classed as partially polar or completely non-polar. Even in such cases the nature of the possible polarity is usually clearly indicated by the behavior of the substance. Thus there is not much question that the oxygen and sulfur atoms of sulfate ion are bound by electron sharing, but no one would hesitate to state that, if the pairs of electrons do not lie equally distant from the two nuclei involved, they must lie closer to the oxygen. To distinguish between this hypothetical type of polarity and the clearly defined polarity exhibited by electrolytes the term **valence number** has been used in this text in discussing the behavior of sulfates and other similar substances as oxidizing agents.

In the use of this term, two points must be remembered. In the first place, since all possible gradations probably exist between polarity and non-polarity, there must also be all possible gradations between cases in which the term valence number and cases in which positive or negative valence should be used. Thus antimony hydroxide may ionize either as an acid or as a base. As a base it yields the ions Sb^{+++} and $3OH^{-}$. Hence antimony is clearly trivalent positive. As an acid it gives the ions $SbO_3^{\equiv}$ and $3H^{+}$. This behavior, on the other hand, might be described by the statement that antimony has the valence number 3+. The second point to bear in mind is that, though the valence number may often show the number of electron pairs shared, it does not always do so. The valence number is used for explaining relative amounts of oxidizing and reducing agents involved in a given reaction, and is found by the simple

such a molecule, the atom which the pair approaches at the moment of greater activity would behave as if it were negative. Attention should also be called to the fact that the term "polar" molecule is used in more than one sense. By some writers, particularly in the United States, the term is used as in the text; by others the term refers to particular physical properties, exhibited for example in the dielectric constant of the substance.

rule given on page 277 without consideration of the possible structure of the compounds.

Limitations of Present Hypotheses of Atomic Structure.—The discussion of atomic structure as related to chemical properties has been limited to the first two series of the periodic system and to the outer groups. None of the hypotheses thus far advanced explains successfully the properties of the heavier atoms, especially those of the inner groups which exhibit many irregularities in behavior, even in valence. This failure is not at all surprising. The problem of atomic structure is a very recent one, and present ideas are only tentative efforts to coordinate known facts. The heavier atoms are necessarily the more complicated ones, and so little is yet known about the factors which determine the behavior of electrons in large, highly condensed aggregates that hypotheses to include these atoms are premature. Langmuir has extended the Lewis hypothesis in a variety of ways, and has attempted to draw a picture which includes the whole periodic system. Others have discussed special phases of the behavior of the more complex atoms, but thus far no view has been sufficiently successful to warrant its inclusion in this text.

Structure of Nuclei and Isotopes.—Since the nuclei of elements undergo no changes in ordinary chemical reactions, there is less material for determining their composition than there is for learning about the arrangements of the outer electrons. Some progress has been made in this direction by considering the distribution of elements in the universe, and by a study of numerical relations in atomic weights. These are too complex for elementary discussion. One point only will be mentioned because of the great influence it has had on our views concerning elements. The nucleus of an element consists of protons and electrons, and its net positive charge is equal to the difference between the number of protons and the number of nuclear electrons. Thus chlorine, with a nuclear charge of 17+, might have a nucleus consisting of 34 protons and 17 electrons. If this were true, its atomic weight should be 34. The nuclear charge might also be accounted for by assuming that the nucleus consists of 35 protons and 18 electrons, or of 37 protons and 20 electrons. In

the former case, the atomic weight would be 35, in the latter, 37. Now the properties of an element are determined by the number of electrons in the outer zone, and not by those in the nucleus. The number of outer electrons is wholly determined by the charge on the nucleus. Hence, all elements consisting of atoms of a given nuclear charge, irrespective of their atomic weight, should have practically identical chemical properties. Such elements would be separable only by methods depending on the mass of the atoms, for instance by differences in rates of diffusion. It has actually been found that chlorine is a mixture of two kinds of atoms—one having the relative mass 35 and the other 37, but both of the same nuclear charge. In this way the fact that chlorine has an **atomic weight which is not a whole number is accounted for.**

Atoms of elements which differ in mass but not in nuclear charge are called **isotopes.** Enough cases have already been investigated by various methods to make safe the statement that all **elements the atomic weights of which are not almost exactly whole numbers consist of mixtures of isotopes.** The discovery of these interesting mixtures resulted from experimental work on radioactivity. The disintegration series shown in Table XVII, page 348, led to the idea that the end product of the uranium series is an isotope of lead. Lead from radioactive sources should therefore have an atomic weight different from that of ordinary lead. As a matter of fact, lead associated with radioactive substances has an atomic weight of 206, whereas the atomic weight of ordinary lead is 207.2. Some elements have many isotopes—mercury has 6 and tin 8.

Atomic Weights and the Origin of Elements.—The discovery that many elementary substances consist of mixtures of isotopes again raises the question of the significance of atomic weights. Again the answer is that their practical value is unimpaired by the new developments. Since isotopes have practically identical chemical properties, they are not separable by natural processes. In any elementary substance found on the earth the relative number of the atoms of each isotope is constant, and the atomic weight is a numerical expression of this relation. The fact that chlorine has an atomic weight 35.46 means that 77 per cent of the atoms have the relative weight 35, and 23 per cent, the weight

37.[1] Moreover, all chemical reactions are carried out with such enormous numbers of molecules that separation of the two types of chlorine atoms by chance is excluded. For these reasons chlorine always reacts as if it consisted of only one kind of atom of atomic weight 35.46. The usefulness of this number in making all sorts of calculations cannot be questioned.

The most important point in this connection is that the elements, although they may be mixtures of isotopes, are each found by the most careful experiments to possess a perfectly definite atomic weight. This statement applies not only to the elements as they are observed in the earth's crust, but also to elements brought to the earth from other portions of the universe by meteors. A possible conclusion from these facts is that the elements have been built up from or formed by decomposition of other elements, and that the different isotopes differ in ease of formation or in stability in such ways that they are always formed in the same proportion. Thus a new field of investigation of the utmost importance and fascination has been opened.[2]

Table XVIII summarizes the results of experimental work thus far done in ascertaining the number of isotopes of the various elements. In the second column is given the atomic number of each element, in the third its atomic weight, and in the fourth the minimum number of isotopes. When only one kind of atom is known for the element, the number of isotopes is given as 1, when two kinds of atoms the number of isotopes is given as 2, etc. The fifth column gives the atomic weights of the isotopes arranged in the order of their abundance. Thus ordinary chlorine consists of the 2 isotopes of atomic weight 35 and 37 respectively; the one with atomic weight 35 is given first because the mixture contains it in the greater amount. Obviously the atomic weights of the elements as found in column

[1] If x is the fraction of the atoms of atomic weight 35:

$$35x + 37\,(1 - x) = 35.46$$

and thus solve for x.

[2] The only elements the atomic weights of which differ in samples of different origin are those which, like lead, are still in the process of formation from radioactive elements. Even for these, the vast bulk of the material is of constant atomic weight.

TABLE XVIII

ISOTOPES

ELEMENT	ATOMIC NUMBER	ATOMIC WEIGHT	MINIMUM NUMBER OF ISOTOPES	ATOMIC WEIGHT OF ISOTOPES IN ORDER OF THEIR ABUNDANCE
Hydrogen	1	1.008	1	1.008
Helium	2	4.00	1	4
Lithium	3	6.939	2	7, 6
Beryllium	4	9.02	1	9
Boron	5	10.82	2	11, 10
Carbon	6	12.000	1	12
Nitrogen	7	14.008	1	14
Oxygen	8	16.000	1	16
Fluorine	9	19.00	1	19
Neon	10	20.2	2	20, 22
Sodium	11	22.997	1	23
Magnesium	12	24.32	3	24, 25, 26
Aluminium	13	26.96	1	27
Silicon	14	28.06	2	28, 29, (30?)
Phosphorus	15	31.024	1	31
Sulfur	16	32.065	1	32
Chlorine	17	35.458	2	35, 37
Argon	18	39.91	2	40, 36
Potassium	19	39.095	2	39, 41
Calcium	20	40.07	(2)	40 (44)
Iron	26	55.84	(2?)	56, (54?)
Nickel	28	58.69	2	58, 60
Zinc	30	65.38	4	64, 66, 68, 70
Arsenic	33	74.96	1	75
Selenium	34	79.2	6	80, 78, 76, 82, 77, 74
Bromine	35	79.916	2	79, 81
Krypton	36	82.9	6	84, 86, 82, 83, 80, 78
Rubidium	37	85.44	2	85, 87
Tin	50	118.70	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Antimony	51	121.77	2	121, 123
Iodine	53	126.932	1	127
Xenon	54	130.2	9	129, 132, 131, 134, 136, 128, 130, 126, 124
Caesium	55	132.81	1	133
Mercury	80	200.6	(6)	(197–200), 202, 204

Taken from Richards. (See References.)

three are the means of the atomic weights of the corresponding isotopes.

Elements.—Obviously the original definition, that elements are homogeneous substances which cannot be decomposed, is no longer strictly tenable, since many elementary substances have been found to be mixtures of isotopes, and some of them suffer spontaneous decomposition. The difficulties are avoided by defining an elementary substance as one which consists of atoms all of which have the same nuclear charge, while compounds consist of atoms which have different nuclear charges. The isotopes of an element are varieties of that element, and the elementary substance in such a case is a unique mixture because of the identity of the properties of its components.

EXERCISES

(1) (*a*) What reasons have been given in the text for the view that all atoms are built up of protons and electrons? (*b*) What additional assumption must be made in order that this hypothesis may be tenable?

(2) Draw schematic figures illustrating the structures of the following atoms according to the Lewis hypothesis: carbon, nitrogen, sodium, silicon, and chlorine.

(3) Explain why magnesium has a valence of 2+, and oxygen a valence of 2−, according to the Lewis hypothesis.

(4) Illustrate the two modes of compound formation, postulated by Lewis, by drawing figures to represent (*a*) magnesium chloride, and (*b*) chlorine molecules.

(5) Explain why, according to the hypothesis discussed in this chapter, sodium is less electropositive than potassium, and chlorine less electronegative than fluorine.

(6) Draw a figure to illustrate the structure of the hydrogen molecule, and another to illustrate the molecule of hydrogen chloride, assuming the latter to be formed by transfer of electrons.

(7) (*a*) Define the terms polar and non-polar compounds as used in this text. (*b*) Explain what is meant by partial polarity.

(8) (*a*) What are isotopes? (*b*) In Table XVII, page 348, are given the products of disintegration of uranium, and the character of the change by which each is formed. Remembering that an alpha change means that the nucleus has lost 2+ charges, and a beta change that the nucleus has gained 1+ charge, calculate the nuclear charge of each of

the decomposition products given. The nuclear charge of uranium is 92. (*c*) Which of these products are isotopes of each other?

REFERENCES

Russell, Bertrand—A. B. C. of the Atom.

Mills, F.—Within the Atom. These two books are written in as simple style as possible to introduce the general reader to the experimental and logical basis of modern hypotheses of atomic structure.

Loring, F. H.—Atomic Theories, takes up several hypotheses of atomic and molecular structure.

Thomson, J. J.—The Electron in Chemistry, deals with both physical and chemical aspects of the subject.

Lewis, G. N.—Valence and the Structure of Atoms and Molecules, deals with the theory outlined in this text.

The last three books are quite technical but contain a great deal of interest to the student of general chemistry.

Richards, T. W.—Chemical Reviews, Vol. I, pages 18–37. This article, already referred to, gives an excellent and simple review of atomic weights and isotopes.

CHAPTER XXV

OXIDES AND OXYGEN ACIDS OF THE HALOGENS

In the chapter on the halogens (Chapter XI, page 146) only the simplest types of halogen compounds were discussed in detail. These compounds are the halogen acids and the halides which may be assumed to be formed by complete transfer of 1 electron from the halogen to the hydrogen or to the metal atom. Consequently the substances are very highly, if not completely ionized in solution, yielding the negative halide ion. Although oxygen and the halogens do not unite directly, oxygen compounds of the halogens may be prepared by indirect methods. Oxygen and halogen atoms are probably bound by sharing of electrons rather than by complete transfer of electrons; but the behavior of the compounds is best interpreted by assigning to the halogen a positive valence number indicating possible displacement of the shared electrons toward the oxygen.

A list of the oxygen compounds and the oxygen acids is given in Table XIX.[1]

The discontinuities in the table are very striking. Fluorine forms no oxides or oxygen acids; this fact is an illustration of the general statement that in an outer group the tendency to form positive ions, or to exhibit positive valence numbers, increases with atomic weight. There is, on the other hand, no explanation or parallel in other groups for the fact that bromine is the only one of the group which, though found in oxygen acids, forms no oxides. In the following discussion only the chlorine

[1] There are of course many compounds which contain oxygen and halogens, other than those given in the table, such as basic halides, sulfuryl fluoride and chloride, etc. The compounds listed in the table are those in which halogen is bound directly to oxygen while in the others oxygen and halogen are both bound to a third atom.

compounds, which are more common than those of the other halogens, will be taken up in detail.

TABLE XIX

OXIDES AND OXYGEN ACIDS OF THE HALOGENS

VALENCE NUMBER OF THE HALOGEN IN THE COMPOUNDS	CHLORINE COMPOUNDS		BROMINE COMPOUNDS	IODINE COMPOUNDS	
1+	Cl_2O Chlorine monoxide	HOCl Hypochlorous acid	HOBr Hypobromous acid	.....	HOI Hypoiodous acid
3+	.....	$HClO_2$ Chlorous acid	.....	.....	.....
4+	ClO_2 Chlorine dioxide	.....	.....	I_2O_4 Iodine tetroxide *	.....
5+	.....	$HClO_3$ Chloric acid	$HBrO_3$ Bromic acid	I_2O_5 Iodine pentoxide	HIO_3 Iodic acid
7+	Cl_2O_7 Chlorine heptoxide	$HClO_4$ Perchloric acid	.....	.....	H_5IO_6 Per-iodic acid

* Iodine tetroxide is usually considered to be a compound in which one of the iodine atoms has the valence number 3+ and the other the valence number 5+ as indicated by the formula $OI(IO)_3$.

Hypochlorous Acid and Chlorine Monoxide.—The fundamental reaction upon which all methods for the preparation of hypochlorous acid are based is that of chlorine with water:

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl \qquad (1)$$

Since equilibrium is reached in this reaction when only very small amounts of hypochlorous acid are formed (page 156), the reaction can be driven to the right only by removing one or another of the reaction products.[1] This is accomplished by passing

[1] Equilibrium conditions for the reaction between bromine and water and iodine and water are briefly described on page 157. In the case of the latter, equilibrium normally lies so far to the left that free iodine may be present even when a moderate excess of a base is used.

the chlorine into a solution of a base rather than into water, because the hydroxide ions of the former remove the hydrogen ions. If sodium hydroxide is used, a mixture of sodium chloride and sodium **hypochlorite,** NaOCl, is obtained. Frequently calcium hydroxide is employed; in this case the hydrogen ion of the hydrochloric acid neutralizes one of the hydroxide ions of the calcium hydroxide, and the hydrogen ion of the hypochlorous acid neutralizes the other. The resulting product is the substance, CaCl(OCl), known as **bleaching powder.** A very convenient method of obtaining hypochlorites consists in the electrolysis of aqueous solutions of chlorides (for example, sodium chloride) in apparatus devised to mix the chlorine obtained at the anode with sodium hydroxide obtained at the cathode. Treating any hypochlorite or bleaching powder with an acid liberates hypochlorous acid, since the latter is very little ionized. Even carbonic acid is strong enough to do this.

All of these methods yield solutions of hypochlorous acid contaminated with chlorides. For most purposes the admixture is of no importance. Pure aqueous solutions of hypochlorous acid are obtained by passing chlorine monoxide into water. The oxide is prepared by the action of chlorine on mercuric oxide:

$$2Cl_2 + HgO \rightarrow HgCl_2 + Cl_2O \quad [2] \qquad (2)$$

$$Cl_2O + H_2O \rightleftarrows 2HOCl \qquad (3)$$

Properties of Chlorine Monoxide and of Hypochlorous Acid.— Chlorine monoxide is extremely unstable; it decomposes explosively as the result of slight mechanical shock. Hypochlorous acid is unknown except in dilute solutions. Even these decompose into hydrochloric acid and oxygen, especially on exposure to light (page 156). Nevertheless, hypochlorites and the acid are of considerable practical importance, because of their usefulness as **bleaching agents** and as **disinfectants.**

Both of these uses depend upon the fact that hypochlorous acid is a strong oxidizing agent. The chlorine with valence

[2] This reaction may be considered a variant of equation (1) in which action to the right is favored by formation of the slightly ionized mercuric chloride and of the volatile chlorine monoxide.

number 1+ has a strong tendency to revert to chloride ion, thus taking up electrons. For example iodides are first oxidized to free iodine and then to iodic acid:

$$\overset{1+}{2HOCl} + \overset{1-}{4NaI} \rightarrow 2NaOH + \overset{1-}{2NaCl} + \overset{0}{2I_2} \qquad (4)$$

$$2 \times 2\epsilon = 4 \times 1\epsilon$$

$$H_2O + \overset{1+}{5HOCl} + \overset{0}{I_2} \rightarrow \overset{5+}{2HIO_3} + \overset{1-}{5HCl} \qquad (5)$$

$$5 \times 2\epsilon = 2 \times 5\epsilon$$

Hypochlorites are in general not as good oxidizing agents as free hypochlorous acid. Consequently, the former are usually acidified before being used. In many cases carbon dioxide absorbed from the air liberates enough of the acid to cause the reaction to proceed. The function of acids in reactions of this sort has already been discussed (pages 283 and 322); with hypochlorites the actual liberation of slightly ionized hypochlorous acid may be an important factor.

Since hypochlorous acid is a strong enough oxidizing agent to injure wool or silk fabrics, its use as a bleach is restricted chiefly to cotton goods. As a disinfectant, it is employed in large amounts to sterilize contaminated water supplies. Aqueous solutions of hypochlorites are used to disinfect certain types of wounds (Dakin's fluid), and bleaching powder, sometimes sold as chloride of lime, is useful as a deodorant.

When hypochlorites are heated they decompose into chlorates. The reaction may be looked upon as an oxidation of hypochlorites by themselves as shown in the equation:

$$\overset{1+}{NaOCl} + \overset{1+}{2NaOCl} \rightarrow \overset{5+}{NaClO_3} + \overset{1-}{2NaCl} \qquad (6)$$

$$4\epsilon = 2 \times 2\epsilon$$

This reaction is the basis for the preparation of chlorates.

The behavior of hypochlorous acid is in many respects identical with that of aqueous solutions of chlorine. Since chlorine fails to display many of its characteristic reactions when perfectly dry, the assumption is frequently made that some of its proper-

ties, such as oxidizing, bleaching, and disinfecting powers are due to the hypochlorous acid formed by the reaction of the chlorine on water.

Chlorates and Chloric Acid.—The method for the preparation of chlorates has already been indicated in equation (6). The hypochlorites are usually not isolated. Instead the water or alkali with which the chlorine reacts is heated to cause immediate formation of chlorates. The chlorine may be used as a gas, or may be generated electrolytically along with the hydroxide, as described in the preparation of hypochlorites. Potassium chlorate is most readily prepared pure, because it is so much less soluble than the corresponding chloride that the two may be easily separated.

Chloric acid may be prepared by the action of dilute sulfuric acid on an aqueous solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2HClO_3 \qquad (7)$$

It is a strong acid. Although more stable than hypochlorous acid, it has not been obtained in the pure condition. Dilute solutions of the acid, prepared by the reaction described, may be concentrated to about 40 per cent by evaporation, but the temperature must be kept below 40° to avoid decomposition. If the solution is warmed or concentrated beyond the limits mentioned, chloric acid decomposes into chlorine dioxide and perchloric acid. This reaction may again be interpreted as an intra-molecular oxidation and reduction of chloric acid:

$$(2+1)\overset{5+}{H}Cl\overset{}{O_3} \rightarrow 2\overset{4+}{Cl}O_2 + \overset{7+}{H}Cl\overset{}{O_4} + H_2O \qquad (8)$$

$2 \times 1\epsilon = 2\epsilon$

Chloric acid is a powerful oxidizing agent. It converts bromine and iodine into bromic and iodic acids respectively. In the course of the action chlorine is liberated.[1] The concentrated (40 per cent) solution acts vigorously with carbon compounds; paper when moistened with it catches fire. The chlorates are more

[1] Part of the chlorine is reduced to chloride:

$$3H_2O + 5HClO_3 + 3I_2 \rightarrow 5HCl + 6HIO_3$$

stable than the free acid, but decompose on heating to give the corresponding chloride and oxygen.[1] Chlorates at elevated temperatures consequently are good oxidizing agents. This accounts for their use in matches, fireworks, and explosives.

Chlorine Dioxide.—Chlorine dioxide, obtained by the decomposition of chlorates, equation (8), is a yellow gas which condenses to a liquid at 10° at atmospheric pressure. At slightly elevated temperatures or in the presence of traces of reducing agents it decomposes with explosive violence into its elements. For this reason chlorates must never be treated with concentrated sulfuric acid, unless only minute amounts of the former are used. The distinctive yellow color and characteristic odor of chlorine dioxide appear whenever a small crystal of a chlorate is treated with either concentrated sulfuric or hydrochloric acid, and the reaction is therefore used as a test for chlorates.[2] The dioxide is, of course, a powerful oxidizing agent. When passed into water, it gives chloric and **chlorous acids** ($HClO_3 + HClO_2$). If a solution of a base is used in place of the water, chlorates and **chlorites** are obtained.

Perchlorates and Perchloric Acid.—When chlorates are cautiously heated, two reactions occur:

$$2KClO_3 \rightarrow 2KCl + 3O_2 \qquad (9)$$

$$4KClO_3 \rightarrow 3KClO_4 + KCl \qquad (10)$$

In the absence of a catalytic agent, and at the lowest possible temperature, the second reaction proceeds more rapidly than the

[1] For the intermediate formation of perchlorates see below.

[2] The action of chlorates on hydrochloric acid is complex. The chloric acid, chlorine dioxide and perchloric acid primarily formed are almost at once decomposed into chlorine. Some oxygen also may be liberated. The action of moderately concentrated hydrochloric acid on chlorates is a convenient method for rapidly preparing a solution of chlorine in water. This solution is contaminated with other chlorine compounds. The method may be used only with small quantities because of the danger of explosions. A moderately safe method of preparing chlorine dioxide is in the action of chlorates on moist oxalic acid:

$$2HClO_3 + H_2C_2O_4 \rightarrow 2ClO_2 + 2CO_2 + 2H_2O$$

Chlorine dioxide is liberated from the mixture at 60°. Explosions do not occur below 100° if organic materials such as cork, rubber, etc., are not allowed to come into contact with the gas.

first. About one-fifth of the chlorate loses all of its oxygen, while the remaining four-fifths decomposes into perchlorate. The latter is separated from the chloride simultaneously formed by solution in water, in which the perchlorate is relatively slightly soluble. From perchlorates the corresponding free acid may be prepared. It is sufficiently stable to be distilled from a concentrated solution at reduced pressure. The solution for this purpose is obtained by passing hydrogen chloride gas into a saturated solution of sodium perchlorate. Sodium chloride precipitates out, and perchloric acid remains in solution.

Although perchloric acid is much more stable than the other oxygen compounds of chlorine, it nevertheless decomposes explosively when heated above about 90°. It is the strongest of the oxygen acids and the least rapid oxidizing agent. Thus it does not oxidize hydrochloric acid in the cold as does chloric acid, nor does it immediately liberate chlorine dioxide when treated with concentrated sulfuric acid. With phosphorus pentoxide it yields the very unstable **chlorine heptoxide,** Cl_2O_7. This substance is the anhydride of perchloric acid, and is sometimes called perchloric anhydride.

Summary of the Oxygen Acids of Chlorine.—The interrelations of the various oxygen acids of chlorine exhibit a number of regularities which are repeated in similar compounds of other elements. **The more oxygen the acids contain,** that is **the higher the positive valence number of the chlorine, the more stable** and **the more strongly acid** they are. The same relationship is exhibited by the oxygen acids of sulfur and of nitrogen. Sulfuric acid and nitric acid are far more stable than sulfurous and nitrous acids, and they are much stronger acids. At the same time, the compound with the highest positive valence number of the " central atom " is the least effective oxidizing agent.[1]

[1] The student is cautioned again not to confuse the "positiveness" of an element with its tendency to form compounds in which it has a high positive valence number. When comparing various elements with each other, we find that the more positive an element, the less acid and the more basic is its hydroxide. But for a given element, the hydroxide in which the element has the lowest positive valence number is the strongest base or the weakest acid. Thus HOCl is a weak acid and $HClO_3$ a strong acid; $Mn(OH)_2$ is a moderately strong base and $HMnO_4$ a strong acid. The two statements are not in

Oxygen Compounds of Bromine and of Iodine.—It is important to note that while chlorine displaces bromine and iodine from bromides and iodides, iodine and bromine displace chlorine from chlorates in acid solution. But this is not at all surprising. Chlorine is the most negative of the three, while iodine is the least; chlorine, on the other hand, has the smallest tendency to form compounds in which it has a positive valence number. The fact that chlorine has the greatest tendency to become negative chloride ion accounts also for the smaller stability and greater oxidizing power of its oxygen compounds. In the free acids these relationships are obscured by formation of complex compounds, but in the case of the salts they are clear. Chlorates are the most readily decomposed, iodates the least readily and so on.

Iodates and bromates are used quite extensively in analytical chemistry, both because of their oxidizing reactions and because they form a large number of insoluble precipitates. They have been very useful in separating the rare earths from each other.

Interhalogen Compounds.—The following compounds are known: Iodine fluoride, IF_5, iodine trichloride, ICl_3, iodine monochloride, ICl; iodine bromide, IBr, and bromine trifluoride, BrF_3. There are reasons to believe that in these compounds the element of higher atomic weight is the positive ion although all of them are little ionized substances. None of them is very stable. Iodine monochloride is the red substance obtained as an intermediate product in the action of chlorine or of hypochlorous acid on iodine. The final product of the reaction is iodic acid, as already mentioned.

the least contradictory. In the first place, the one statement deals with corresponding compounds of different elements, while the other deals with different compounds of the same element. In the second place, neither the number of positive or negative charges which an atom may acquire nor the magnitude of the positive valence number is directly related to positiveness or negativeness. It has already been shown in general, that the larger the number of charges, the less is the tendency to assume the charge.

The fact that the oxygen acid in which the element of variable valence has the higher valence number is the less effective oxidizing agent, is unquestionably related to the fact that it is the most stable acid. The more stable the acid, the less complete, under normal conditions, are the reactions of the type used to explain the effect of acids on oxidizing agents. (See pages 283 and 322.)

EXERCISES

(1) Make a list of properties which show that the elements of the halogen group become less electronegative with increase in atomic weight. Use the data given in Chapter XI and this chapter.

(2) Make a list of properties which show that the elements of the group become more electropositive with increase in atomic weight.

(3) How does fluorine react with water?

(4) Show how equation (1) may be balanced by the electronic method on the assumption that chlorine oxidizes and reduces itself.

(5) Devise a plan for an apparatus in which chlorine obtained at the anode by electrolysis of sodium chloride solution may be mixed with sodium hydroxide obtained at the cathode without use of mechanical mixing devices. (See page 376.)

(6) What is the evidence that hypochlorous acid is an extremely weak acid?

(7) Using the method employed for sulfates and nitrates explain why hypochlorites are better oxidizing agents in acid than in neutral or alkaline solutions.

(8) How would you change the device planned in answer to question 5, in order to produce chlorates from chlorides?

(9) Suggest a method for preparing $Ba(ClO_3)_2$ to be used in the preparation of chloric acid. Why does the reaction between barium chlorate and sulfuric acid (equation 7) go to completion?

(10) Write the equation for the reaction between chloric acid and iodine in which chlorine is liberated and iodic acid formed.

(11) In what respects are chlorine dioxide and nitrogen tetroxide similar?

(12) What is the advantage of distilling perchloric acid at reduced pressure?

(13) Judging from the final products of the action of heat on chlorates, what must the effect of heat on perchlorates be?

(14) Using the electronic method balance the equation for the preparation of perchlorates from chlorates.

REFERENCES

Rogers—Industrial Chemistry (1921). Pages 274–280.

Martin—Chlorine and Chlorine Products (1915). Chapters IV and V both deal with the manufacture and uses of the compounds mentioned in this chapter of the text.

CHAPTER XXVI

THE SIXTH OUTER GROUP OF THE PERIODIC SYSTEM

Oxygen and sulfur are by far the most important elements of the sixth outer group of the periodic system. The remaining two, selenium and tellurium, although not rare, are much less abundant. Selenium is occasionally found free together with native sulfur or in combination mixed with corresponding sulfur compounds like pyrite (FeS_2). Consequently, it is often deposited with the "flue dust" in the stacks of sulfur burners used in the production of sulfur dioxide for sulfuric acid manufacture. Tellurium is associated chiefly with gold, silver, and bismuth ores. Both elements are also obtained as by-products in the electrolytic refining of copper. Selenium is used in small amounts for the production of red and violet glass and enamels; no applications of tellurium are of importance.

Oxygen and sulfur have already been discussed in detail, but not from the point of view of the periodic system. In this chapter they will be reviewed briefly, together with the two less common elements, not as individuals, but as members of a group.

Physical Properties of the Elements.—The differences in physical properties of the elements of the group are brought out in the table of their boiling and melting points.

TABLE XX

Melting and Boiling Points of the Elements of the Sixth Group

	Oxygen	Sulfur	Selenium	Tellurium
Melting point *....	−227°	+112°	+217°	+455°
Boiling point.....	−182°	+444.5°	+688°	+1390°

* The melting points of sulfur, selenium, and tellurium are given for the modifications stable at the lower temperatures.

A great difference between oxygen and the other elements is displayed in the data of the table. But this difference is shown even more markedly by other physical properties. Oxygen is very slightly colored, if at all, even in the liquid condition; sulfur exists in yellow and red modifications, selenium in red and gray ones, and tellurium in a white, semi-metallic and in gray and brown forms. Oxygen molecules are diatomic; ozone is a triatomic modification of the element. The common soluble varieties of sulfur have a molecular weight corresponding to the formula S_8, and sulfur vapor near the boiling point has the same formula but undergoes dissociation into S_2 as the temperature is raised. Selenium is like sulfur in this respect, except that in certain solvents and at high temperatures, dissociation finally leads to the formation of free atoms. Very little is known of the modifications and molecular weight of tellurium.

The various modifications of selenium closely resemble those of sulfur in some ways, but there are two outstanding differences. The transformation of the different varieties of selenium into each other is very slow, so that amorphous glassy masses are often obtained when molten selenium is cooled. In contrast to the amorphous forms of sulfur which go over to the stable crystalline forms rather quickly, those of selenium persist in the glassy state for indefinite periods at room temperature. In the second place, all of the modifications of selenium are converted at somewhat elevated temperatures into the stable, semi-metallic gray variety for which sulfur has no analogue.

Gray selenium has one very unusual property. It possesses moderate electrical conductivity which increases markedly when the substance is exposed to light. The change is proportional to the intensity of the illumination. When the light is withdrawn, the conductivity returns to its original value. The cause of the phenomenon is unknown, but many attempts have been made to utilize it. Light buoys have been constructed with "selenium cells" to control the flow of gas so that the light is shut off during the day and burns at night. Devices for sending pictures by telegraph and others of similar nature have been suggested, but most of them have not yet been perfected.

The comparison of the physical properties of the elements

illustrates two regularities of the periodic system. In the first place, the differences between oxygen and sulfur, the first two members of the group, are greater than those between any succeeding pair of elements. In the second place, although no one of the elements is characteristically metallic, rudiments of metallic properties appear in selenium and become even more pronounced in tellurium—in other words, the elements become more metallic with increase in atomic weight.

Compounds of the Elements with Metals and with Hydrogen.—In their behavior toward the metals the elements of the group are very much alike. Metals like iron, which burn in oxygen, also burn in sulfur vapor, or, when mixed with solid sulfur and heated, react so vigorously that the mass is brought to a bright glow. Other metals which rust slowly in air can be made to combine with sulfur, selenium, or tellurium by merely being ground with these elements. The resulting compounds (oxides, sulfides, selenides, and tellurides, respectively) have similar properties. Thus the solubilities of the selenides and tellurides are of the same order of magnitude as those of the corresponding oxides and sulfides. In general, however, the oxides are less deeply colored, while the tellurides have the darkest colors.

The similarities extend to the chemical properties also. When sulfides are treated with strong acids, the weak acid hydrogen sulfide is set free unless the sulfide is too insoluble to react. Similarly the weak acid water is formed when oxides are treated with strong acids. In other words, just as sulfides are the salts of the acid, hydrogen sulfide, so oxides are the "salts" of the weak acid hydrogen oxide, or water. The analogy may be carried further. Hydrogen sulfide is a somewhat stronger acid than water, and must therefore displace water from its salts, the oxides. Hence reactions like the following occur:

$$CaO + H_2S \rightleftarrows CaS + H_2O$$

But hydrogen sulfide is not a very strong acid, and therefore the reaction must also go somewhat to the left; that is, the sulfides are hydrolyzed. Selenides and tellurides behave much as do oxides and sulfides, but the strengths of hydrogen selenide and

hydrogen telluride as acids are not known with any degree of accuracy.

Sulfides, selenides, and tellurides, as well as the corresponding hydrogen compounds, are strong reducing agents. This is due to the fact that the ions, $S^{=}$, $Se^{=}$, and $Te^{=}$, readily lose the two extra electrons to which they owe their charge. The reducing properties increase in the order given. Oxides and water, on the other hand, do not possess reducing properties because oxide ions retain the extra electrons much more tenaciously. Oxygen is therefore the most and tellurium the least electronegative element of the group, in perfect agreement with the regularities of the periodic system.

This decrease in "negativeness" also explains why water is the most stable of the hydrogen compounds of the group. In these compounds the elements in question are the negative constituents, and the more strongly they retain their negative charge the more stable are the compounds. Thus water is formed from its elements very readily, and is very stable. The reaction between sulfur and hydrogen, on the other hand, is slow under all conditions, and hydrogen sulfide is completely decomposed at moderately high temperatures. Hydrogen selenide is even less stable, while hydrogen telluride decomposes spontaneously in the presence of moisture.

The sulfides of the alkali metals react with sulfur to form polysulfides, and the corresponding oxides unite with oxygen to give peroxides. The resulting compounds have many properties in common. Thus both classes are reducing agents, because the polysulfide ions and peroxide ions readily give up electrons:

$$S_2^{=} \rightarrow 2S + 2\epsilon, \quad \text{and} \quad O_2^{=} \rightarrow O_2 + 2\epsilon$$

But both classes of compounds may also act as oxidizing agents, because the polysulfide and peroxide ions gain two electrons each in going over to the simple sulfide or oxide ions respectively:

$$2\epsilon + S_2^{=} \rightarrow 2S^{=}, \quad \text{and} \quad 2\epsilon + O_2^{=} \rightarrow 2O^{=}$$

Polysulfides when treated with acids give hydrogen polysulfides; peroxides under similar conditions give hydrogen peroxide.

These hydrogen compounds are very unstable, decomposing spontaneously with more or less speed, depending on the temperature, the alkalinity of the medium, or the presence of catalytic agents.

Compound Oxygen Ions and Their Analogues.—Oxygen has a very pronounced tendency to enter into compound ions such as nitrate, phosphate, etc. Sulfur, selenium, and tellurium not only form completely analogous ions, but the oxygen atoms in such ions may be replaced, one by one, by atoms of the other elements. Thus the following series of compounds has been prepared:

Na_3PO_4, Na_3PO_3S, $Na_3PO_2S_2$, Na_3POS_3, and Na_3PS_4

Corresponding selenium compounds are known, although the selenium series has not been obtained complete; and tellurium also forms similar ions. In general, the compound ions of this type containing oxygen are the most numerous and stable, while those of tellurium are the least stable.

Compounds in which the Elements of the Group Have a Positive Valence Number.—In the discussion of partial polarity (page 367) it was pointed out that, if there is any polarity at all in such ions as nitrate, phosphate, sulfate, etc., the oxygen must be considered the more negative constituent. Hence, it may be said that in all of the compounds thus far discussed in this chapter, oxygen and the other elements of the group under consideration are the negative constituents. Oxygen possibly forms no compounds of any other type, although in some cases positive oxygen has been postulated by some investigators. But the situation is quite different for the other elements of the group; in many of their most important compounds, positive valence numbers may be assigned to them. Thus they form the following halogen compounds:

TABLE XXI

HALOGEN COMPOUNDS OF THE GROUP

SF_6		SeF_6	SeF_4		TeF_6	TeF_4		
SCl_4	S_2Cl_2		$SeCl_4$	Se_2Cl_2		$TeCl_4$	$TeCl_2$	
	S_2Br_2		$SeBr_4$	Se_2Br_2		$TeBr_4$		
						TeI_4		

These halides react with water to give the corresponding halogen hydrides, that is, compounds in which the halogen is unquestionably negative. This is, of course, not conclusive evidence that the halogen atoms have the same polarity in the compounds mentioned in the table. But it is at least indicative that any partial polarity, which may exist, is of such character that the elements under consideration are the positive constituents. It is therefore of interest to note that tellurium is the only one which combines with iodine; a further indication that tellurium is the most electropositive element of the group.

The Oxygen Compounds of Sulfur, Selenium, and Tellurium. —Selenium and tellurium, like sulfur, form both di- and trioxides. These oxides react with water to give selenious and tellurous, and selenic and telluric acids respectively. These compounds are analogous to sulfurous and sulfuric acids, except that tellurium in addition to forming H_2TeO_4 also gives H_4TeO_5 and H_6TeO_6 by taking on 1 or 2 extra molecules of water. The acids of selenium and tellurium are weaker than the corresponding acids of sulfur; this is particularly true of the tellurium compounds, for telluric acid is a fairly weak acid and tellurous acid actually displays basic properties. Again this is an indication of increasing positiveness with ascending atomic weights, since oxygen acids of the more positive elements are always weaker acids and more likely to be basic than those of less positive elements.

Since selenium and tellurium seem in so many respects to be more electropositive than sulfur, it might be expected that selenic and telluric acids would not be as good oxidizing agents as sulfuric acid. That is, it might be supposed that sulfur in sulfates would have a greater tendency than selenium or tellurium in the corresponding compounds, to revert to the negative or neutral condition by taking up electrons. As a matter of fact, however, selenic and telluric acids are better oxidizing agents than sulfuric acid. This is, in part, probably due to the fact that the heavier elements of a group generally tend to assume the intermediate valence numbers. Consequently, selenium and tellurium are more easily reduced than sulfur from compounds in which their valence number is 6+ to those in which it is 4+. But this explanation is not completely satisfactory, because it

does not account for the fact that selenious and tellurous acids are also stronger oxidizing agents than sulfurous acid. Thus very weak reducing agents can be used to prepare elementary selenium or tellurium from the corresponding dioxides, whereas moderately strong reducing agents are required to reduce sulfur dioxide or sulfurous acid. No adequate explanation can be given for the discrepancy.

EXERCISES

(1) What is the evidence that oxygen is the most electronegative element of the group?

(2) Point out the analogies between sulfides and oxides.

(3) What is meant by the statement that oxides may be considered a salt of the weak acid water?

(4) Explain why peroxides may act both as reducing and as oxidizing agents.

(5) Explain the spontaneous decomposition of hydrogen peroxide on the assumption that it is a case of "self-oxidation" and balance the equation for the decomposition on this assumption.

(6) (*a*) Contrast the oxygen acids of sulfur with those of selenium and of tellurium. (*b*) Which of the differences are in accordance with the regularities of the periodic system, and which are not?

CHAPTER XXVII

THE NITROGEN GROUP

The elements of the fifth outer group of the periodic system constitute an unusually coherent family. The gradations in properties are regular, and in most respects agree closely with the generalizations mentioned in the discussion of the periodic system. The first element of the group, nitrogen, differs quite decidedly from the others, as is also the case in all of the other groups. Aside from theoretical considerations the group is also important because of the practical value of each of its elements. **Phosphorus**, like nitrogen, is a constituent of all living organisms and is therefore found in all fertile soil. Large quantities of phosphates are used annually in fertilizers. Phosphorus sulfide today replaces the free phosphorus formerly employed in matches. Small amounts of the free element are used medicinally. Some alloys contain small percentages of phosphorus which imparts hardness to the metal. **Arsenic** also is used in alloys as a hardening agent. Its compounds are employed as insecticides, as valuable drugs, and in the manufacture of opaque glass and enamels. **Antimony** compounds are among the oldest of drugs. The element is employed very largely in making relatively soft alloys such as are used in bearings and type metal. The most important use of **bismuth** is likewise in alloys, of which, for example, the low melting plugs of automatic sprinklers are made. It too is used medicinally. The discussion of the properties of the elements will afford opportunity for a review of the properties of nitrogen, and for further study of the periodic system.

Preparation of the Elements.—Arsenic, antimony, and bismuth occur most commonly as sulfides. These may be heated in air to convert them to the respective oxides, which are reduced by carbon to the free elements. Arsenic is found also in large

amounts as arsenical pyrites, or mispickel, FeAsS, which when heated gives ferrous sulfide and free arsenic. Antimony may be prepared in similar fashion by heating the sulfide with iron:

$$Sb_2S_3 + 3Fe \rightarrow 3FeS + 2Sb \qquad (1)$$

The chief sources of phosphorus are minerals, the essential component of which is calcium phosphate. This substance is reduced to elementary phosphorus only with considerable difficulty. It was formerly converted by treatment with sulfuric acid into phosphoric acid which was then reduced with carbon. This process has been displaced by the electric furnace. Calcium phosphate is mixed with carbon and silicon dioxide, and the mixture introduced into the furnace. The passage of an alternating current through the material between carbon poles produces a very high temperature, under the influence of which the following reaction occurs:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + P_2 \qquad (2)$$

Modifications of the Elements.—Phosphorus, arsenic, and antimony exist in a number of solid modifications differing markedly in appearance and physical properties. Nitrogen solidifies at a very low temperature, and little is known about the element in the solid state, but at least one active modification of the gas can be prepared. Bismuth has been found in only one solid form, but a careful study might reveal the existence of others. An understanding of the relations between the various modifications is essential for a proper conception of the chemical behavior of the elements of the group.

When **phosphorus** vapor is suddenly cooled (for example, by passing it into water) it solidifies to a white mass consisting of soft, wax-like crystals. The substance, known as **white phosphorus,** melts at 44°, and boils at approximately 290°; but even at room temperatures it has an appreciable vapor pressure, and evaporation is readily noticeable. Since it is very poisonous, its great volatility makes it dangerous to work with. The vapors ignite spontaneously in air, so that white phosphorus very easily catches fire, and must be kept under water, in which

it is insoluble. It is easily soluble in carbon disulfide. In this solvent and in the vapor at temperatures up to 1500°, its molecular weight corresponds to the formula, P_4; at higher temperatures it dissociates to P_2. On exposure to light, white phosphorus gradually becomes yellowish. The change is due to the transformation of the phosphorus into a red mass, and is greatly accelerated by heating the substance out of contact with air. The red material, which is called **red phosphorus,** is not uniform. Its color and density vary in different samples. It always contains small amounts of unchanged white phosphorus, but it is largely amorphous. The nature of red phosphorus is most satisfactorily interpreted by assuming that it is a transition form between white phosphorus and another crystalline modification, called **violet phosphorus.**[1] The latter may be obtained pure by dissolving red phosphorus in molten lead and allowing the mixture to crystallize, or by separating red phosphorus into its components by suspending it in water and allowing the heavier violet modification to settle out. The process must be repeated many times to effect complete separation. Violet phosphorus melts at approximately 600°, and is much less volatile and active than the white form. It is insoluble in all common solvents, and must be heated to 240° before it catches fire. The red variety, being a mixture, has no definite melting point. Its properties are essentially those of violet phosphorus, since any white phosphorus it may contain is completely enclosed by the particles of the violet modification. The red and the violet forms are practically non-poisonous, probably because of their inactivity and insolubility.

Red or violet phosphorus may be prepared by heating white phosphorus, but the white form can be prepared only from phosphorus vapor. White phosphorus is at all temperatures a **metastable** modification, existing temporarily because of the slowness of the change into the stable violet form. Phosphorus is, in other words, monotropic in contrast to sulfur, which is allotropic. (See page 245.) Whenever a metastable form goes over into a stable variety, heat is given out. The metastable form is the more active chemically. Other forms of phosphorus besides those

[1] Violet phosphorus is also called Hittorf phosphorus after its discoverer.

mentioned have been described, but they are not well known and may be merely varieties of those already discussed.

Like phosphorus, **arsenic** exists in two definite modifications and a number of transition forms. **Yellow arsenic,** obtained by passing arsenic vapor into carbon disulfide at $-70°$, is very volatile and very reactive. Unlike white phsophorus, yellow arsenic is very readily transformed into the stable, **metallic form.** The latter is much less volatile and reactive than the former. If the transformation takes place under such conditions that the stable modification is formed in very small particles, the resulting material has a **grey** appearance, and is not distinctly crystalline. Since this is the most common form, arsenic is often described as "semi-metallic." The behavior of **antimony** is much like that of arsenic, except that the **yellow** variety is even more rapidly transformed into the **metallic** one, and is very difficult to obtain. Even at $-70°$ in the dark it is converted into the stable form in a few hours. Antimony exists, however, in two metallic modifications. The one known as **explosive** antimony is (like yellow antimony) metastable; a slight scratch or blow causes it to go over to the stable metallic form very suddenly and with the evolution of a very considerable amount of heat.[1]

It is obvious from the preceding discussion that a comparison of the behavior of these elements must be made with due regard to the existence of the various modifications. Even then misleading conclusions may readily be reached. Judging by the properties of the metastable forms, it might be concluded that phosphorus is less reactive than antimony or arsenic, while the opposite conclusion would result from a comparison of the stable modifications. The one known form of bismuth is, of course, the stable modification and the element on this account appears in many respects much less reactive than the others.

Properties of the Elements.—The preceding discussion indicates clearly that with increasing atomic weight the elements become more metallic and therefore more electropositive. Nitrogen and phosphorus have no metallic modifications; yellow

[1] The preparation of explosive antimony and a number of interesting lecture experiments are described in detail by Cohen and Ringer, Zeitschrift für physikalische Chemie, **47**, 22.

antimony is transformed more easily than yellow arsenic into a metallic form; bismuth is known only as a metal. Nevertheless not even the metallic modifications possess metallic properties in the highest degree. Arsenic, antimony, and bismuth in their metallic forms are brittle, whereas a high degree of ductility and tenacity characterizes the typical metals.

The elements of the group, except nitrogen, react readily with oxygen, the halogens, and sulfur. When the active modifications are used the reactions are spontaneous and often violent; with the less active modifications heat is required to start the reactions. On the other hand, the elements of the group also form compounds with electropositive elements such as hydrogen and many metals.

The Hydrides of the Nitrogen Group.—Hydrides whose formulae are analogous to that of ammonia are known for all of the elements of the nitrogen group.

Phosphine, PH_3, may be prepared by the action of calcium phosphide, Ca_3P_2, on water, or of yellow phosphorus on alkalies, such as sodium hydroxide:

$$3KOH + P_4 + 3H_2O \rightarrow \underset{\text{potassium hypophosphite}}{3KH_2PO_2} + PH_3 \qquad (3)$$

It is obtained also when phosphorous acid is heated:

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3 \qquad (4)$$

None of these methods yields pure phosphine. It is always contaminated with another hydrogen compound of phosphorus, P_2H_4, which is spontaneously inflammable in air. The heat developed by the burning of the traces of P_2H_4 sets fire to the phosphine. Pure phosphine does not catch fire in air until heated to 150°.[1]

Phosphine is **more readily decomposed** into its elements than is ammonia. Although ammonia is an exceedingly **weak acid,** phosphine seems to be even weaker. Its salts, such as calcium

[1] In addition to PH_3 and P_2H_4, phosphorus forms two other hydrides, $P_{12}H_6$ and P_9H_2 which are solids. They are formed as the result of the decomposition of P_2H_4 in the absence of air.

phosphide, are completely hydrolyzed by water.[1] Phosphine is a **powerful reducing** agent. Unlike ammonia, it burns readily in air; it reduces strong oxidizing agents such as permanganates and chromates as well as some of the less powerful ones like silver nitrate. The **poisonous character** of phosphine is possibly due to its reducing action. It has a characteristic, unpleasant odor. It is only **slightly soluble** in water and has very little tendency to combine with hydrogen or other positive ions—characteristics which further differentiate it from ammonia. **Phosphonium compounds** are formed only at very low temperature or by precipitation from solution. Thus when phosphine is passed into a saturated solution of hydrogen iodide or bromide, phosphonium iodide or bromide, PH_4I or PH_4Br, is precipitated.[2] Water decomposes the phosphonium salts at once into phosphine.

Arsine, AsH_3, may be prepared by the action of water on arsenides. It is most commonly obtained by the reduction of any arsenic compound in acid solution by zinc or some other of the more active metals. This mode of formation is of importance for two reasons. In the first place, arsine is an **extremely poisonous** gas. Many metals, as well as most of the acids of commerce, contain arsenic as an impurity. In the interaction of such metals and acids, arsine is likely to be produced. Inhaling even very small amounts of the gas may be fatal, and this fact should be remembered in the preparation of hydrogen. Unless the metals and acids used are known to be free from arsenic, the

[1] Compounds to which the name "phosphide" has been applied may sometimes be precipitated even from aqueous salt solutions by the action of phosphine. It is possible that exceedingly insoluble phosphides might not be hydrolyzed. But probably it is more likely that the compounds precipitated by phosphine are not phosphides (in the sense used in this text) but compounds analogous to alloys. This interpretation is borne out by the fact that in many of these supposed phosphides, the elements combined do not display their normal valences.

[2] The preparation of phosphonium chloride, which is more soluble than the corresponding iodide or bromide, requires the use of a solution of hydrogen chloride saturated under pressure. Phosphonium sulfate and hydroxide have been prepared at low temperature but they are even more unstable than the other substances mentioned. Organic phosphonium compounds are fairly stable.

hydrogen should be passed through an alkaline permanganate solution before it is allowed to escape into the air. The production of arsine by the action of zinc on acid solutions containing arsenic is used in the Marsh test, which is the most delicate method of finding traces of arsenic.[1]

Arsine has a strong garlic-like **odor.** It is even more **readily decomposed** into its elements than is phosphine, and **burns** in air. In arsine, the **acid character** of the hydrogen has almost disappeared for metallic arsenides cannot be precipitated from aqueous solutions. They are obtained by action of arsenic on the metals. Arsine is a very **powerful reducing agent,** is very **insoluble in water,** and displays practically no tendency to form compounds analogous to ammonium salts.[2]

Stibine, SbH_3, is best prepared by the action of dilute hydrochloric acid on an alloy of antimony and magnesium in the absence of air. It **decomposes spontaneously** into its elements. In all of its properties it is very similar to arsine. **Bismuth hydride,** BiH_3, is very little known. It has been obtained in traces by a method analogous to that used for the preparation of stibine. It is unquestionably the least stable hydride of the group.

A comparison of the hydrides of the group is an excellent illustration of the regularities characteristic of outer groups in the periodic system. With increase of atomic weight, the hydrides become less stable, less acidic, better reducing agents, and more poisonous. These differences are all unquestionably related to a **decreasing tendency of the elements to be electronegative.** The elements of the group are the negative constituents of the hydrides; consequently the less negative the element is the more readily should the hydride decompose, and the more

[1] In the Marsh test, the hydrogen generated by the action of zinc on an acid solution of the material to be tested is passed through a heated glass tube. Arsine, if present, is decomposed, and the resulting arsenic is deposited on the walls of the tube in the form of a mirror. Various modifications of the Marsh test are also in use in which arsine is detected by its action on silver nitrate, or mercuric chloride or bromide.

[2] A few organic arsonium compounds are known. Likewise some of the complex compounds which arsine forms with mercury salts, etc., may be of the ammonium type.

readily should it act as a reducing agent by loss of electrons. The increase in poisonous properties is probably closely related to the increase in reducing power. Furthermore, it is a matter of experience, rather than of theory, that the less electronegative or the more electropositive an element, the less acidic is its hydride. Thus the hydrides of the halogens are the strongest acids, whereas the hydrides of the alkali and alkaline earth group metals possess no acid properties whatever.[1] The decreasing ability of the hydrides of the nitrogen group to unite with positive ions (to form compounds analogous to ammonium salts) is probably not related to the change in electronegative character, nor is it a characteristic which is repeated in other groups.

Oxides.—Phosphorus, arsenic, antimony and bismuth form trioxides and pentoxides.[2] The trioxides may all be prepared by direct union of the elements. In preparing phosphorus trioxide an excess of phosphorus must be used, as the trioxide reacts very readily with oxygen to form the pentoxide, which is the normal product formed by burning phosphorus in air or in oxygen. The other pentoxides of the group cannot be prepared by direct union of the elements.

A number of differences between these oxides and those of nitrogen are of interest. In the first place nitrogen displays towards oxygen every possible valence number from 1+ to 5+ while the other elements of the group have in their oxides only the valence numbers 3+ or 5+. All the oxides of nitrogen are gases; the oxides of the other elements are solids. Only the trioxides of phosphorus, arsenic and antimony, and the pentoxide of phosphorus are volatile even at high temperatures.

[1] See pages 482 and 492.

[2] The vapor densities of the oxides which are sufficiently volatile for measurement indicate that the formulae of the trioxides and the pentoxides are E_4O_6 and E_4O_{10}, rather than E_2O_3 and E_2O_5 respectively. The symbol E represents any one of the elements named above. At high temperatures the compounds are dissociated into the simpler molecules. For this reason the simpler formulae, which are generally used, have been retained in this text. Compounds of the formula P_8O_{16}, i.e. $(P_2O_4)_4$, etc., exist. These are not analogous to NO_2, but seem to be formed by union of the trioxide and pentoxide. In the case of arsenic and bismuth, the supposed "tetroxides" are really mixtures of the lower and higher oxides.

The oxides of nitrogen are readily decomposed by heat. Both of the oxides of phosphorus and the trioxides of the other elements in the group are very stable.[1] Since nitrogen, the first member of the group, is the most electronegative its oxides, in which nitrogen has a positive valence number, should be the least stable.

The oxides of phosphorus occupy an exceptional place in their **action toward water.** Nitrogen pentoxide and trioxide react very rapidly with water to form nitric and nitrous acids, even though these acids, particularly the latter, are not very stable; the oxides of arsenic react much more slowly; those of antimony and of bismuth do not react with water at all. The oxides of phosphorus ought to lie between those of nitrogen and arsenic in this respect. As a matter of fact phosphorus pentoxide has an extraordinary avidity for water. It is on this account one of the best **drying** agents. The acid formed by union of the oxide with water is very stable; it can be dehydrated and reconverted to the oxide only with the greatest difficulty.

Oxygen Acids (Hydroxides) of the Group.—Nitrogen pentoxide reacts with 1 molecule of water to form nitric acid. In the same say, phosphorus pentoxide unites with water giving **metaphosphoric acid:**

$$P_2O_5 + H_2O \rightarrow 2HPO_3 \qquad (5)$$

The metaphosphoric acid, however, reacts further with water; the reaction is accelerated by rise in temperature and by the presence of strong acids like nitric acid. An additional molecule of water is taken up to form **ortho phosphoric** acid:

$$HPO_3 + H_2O \rightarrow H_3PO_4 \qquad (6)$$

Had all of the phosphorus pentoxide, originally used, been converted into orthophosphoric acid, 3 molecules of water would have been required per molecule of pentoxide. Another acid, **pyrophosphoric acid,** may be considered the product of the reaction of the pentoxide with 2 molecules of water:

$$P_2O_5 + 2H_2O \rightarrow H_4P_2O_7 \qquad (7)$$

[1] The pentoxides of arsenic, antimony, and bismuth are decomposed to the trioxides by heat.

When heated, 2 molecules of orthophosphoric acid first lose 1 molecule of water (213°) to give 1 molecule of pyrophosphoric acid, which when further heated (400°) loses another molecule of water and gives 2 molecules of metaphosphoric acid:

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

$$H_4P_2O_7 \rightarrow 2HPO_3 + H_2O$$

The latter can be volatilized undecomposed at red heat.

Since orthophosphoric acid can yield 3 hydrogen ions per molecule it may give rise to three types of salts—the **primary** orthophosphates in which only 1 hydrogen ion is replaced by a metal ion, the **secondary** orthophosphates in which 2 hydrogen ions, and the **tertiary** orthophosphates in which all 3 are replaced. In the case of pyrophosphoric acid, the possibilities are still more numerous. It is evident, therefore, that a great variety of phosphates (that is, of salts in which phosphorus has the valence number 5+) is possible. For this reason a special section is devoted to them.[1]

Phosphorus trioxide also unites with more water than does nitrogen trioxide, giving **phosphorous acid,** H_3PO_3. An acid with less water, HPO_2, analogous to nitrous acid, also probably exists. Of the 3 hydrogens of phosphorous acid, only 2 are replaceable by metal ions:

$$2NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_2O \qquad (8)$$

Phosphoric acid is a much weaker acid than nitric acid. This agrees with the generalization that the more electropositive an element the less acidic and more basic is its hydroxide. Phosphoric acid does not, however, display any basic properties. Phosphorous acid is still weaker than phosphoric acid, and weaker than nitrous acid. Again the differences are in full agreement with generalizations already discussed. Phosphorous acid is weaker than phosphoric because in the former the valence

[1] Salts of the hypothetical triphosphoric and tetraphosphoric acids $H_5P_3O_{10}$ and $H_6P_4O_{13}$, are known, but are not discussed in this text. The substances, hypophosphorous and hypophosphoric acids, H_3PO_2 and H_2PO_3, are also omitted.

number of the phosphorus is 3+ whereas in the latter it is 5+; phosphorous acid is weaker than nitrous acid because phosphorus is a more electropositive element than nitrogen. Phosphoric acid does not act as an oxidizing agent. Since phosphorus is more electropositive than nitrogen, phosphorus compounds in which the element has a positive valence number should have a smaller tendency to take up electrons than do corresponding nitrogen compounds. The latter should therefore be the better oxidizing agents. But the complete disappearance of oxidizing power in phosphoric acid is unexpected, and is probably due to the same cause which produces the unusual tendency of phosphorus pentoxide to unite with water. Phosphorous acid, like nitrous acid, is a moderately strong reducing agent, showing that the valence number of phosphorus has a considerable tendency to go from 3+ to 5+. The reducing action is illustrated by the behavior of the acid towards iodine:

$$H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2HI \qquad (9)$$

It also reduces acid permanganate solutions to manganous salts.

The **arsenic acids,** $HAsO_3$, H_3AsO_4, and $H_4As_2O_7$, and arsenous acid, H_3AsO_3 or $HAsO_2$ are much like the corresponding acids of phosphorus. They are more unstable, more readily decomposed into their respective oxides, and are weaker acids, as is to be expected. Arsenous acid, in fact, exhibits slight basic properties. When it is treated with a large excess of hydrochloric acid, arsenous chloride is formed.[1] The action may be written:

$$As(OH)_3 + 3HCl \rightarrow AsCl_3 + 3H_2O \qquad (10)$$

Another illustration of the basic character of the acid is the formation of arsenous sulfide:

$$2As(OH)_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O \qquad (11)$$

[1] When solutions containing arsenous acid and hydrochloric acid are heated, arsenous chloride may be given off with the steam. Arsenous chloride is a poisonous substance, and care must be taken not to inhale the vapors from such a solution.

On the other hand its acid properties are illustrated by the formation of **arsenites:**

$$H_3AsO_3 + 3NaOH \rightarrow Na_3AsO_3 + 3H_2O \qquad (12)$$

The formula may be written either $As(OH)_3$ or H_3AsO_3 to illustrate the one or the other mode of action.[1]

In arsenic acid, the ability to act as an oxidizing agent again appears. Hydrogen sulfide, passed into a heated solution of the acid, is oxidized to sulfur and arsenous acid is formed. The latter at once reacts to give the sulfide:

$$2H_3AsO_4 + 2H_2S \rightarrow 2H_3AsO_3 + 2S + 2H_2O \qquad (13a)$$

$$2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O \qquad (13b)$$

Another illustration is the reduction of arsenic acid to arsine by zinc and the other more active metals. Arsenous acid, like nitrous acid, may act either as a reducing or an oxidizing agent. Thus stannous chloride causes deposition of free arsenic from solutions of arsenous acid, and zinc liberates arsine. In these actions the valence number of arsenic changes from 3+ to 0 or to 3−; arsenous acid is an oxidizing agent. Its reducing action is shown in the reaction with iodine:

$$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2HI \qquad (14)$$

But the tendency of arsenic to go over into the compounds in which its valence number is 5+ is not so great as that of nitrogen or phosphorus. This is shown by the fact that the reaction with iodine is reversed in acid solutions. It is to be noted that the acids of arsenic, like **all arsenic compounds, are extremely poisonous.**

The **acids of antimony** are unstable. Attempts to liberate them from their salts lead to the precipitation of mixtures of the oxides with varying amounts of water. From the formulae and behavior of the oxides and of the salts, the momentary existence of acids with formulae corresponding to those of

[1] Arsenic acid also reacts with hydrogen sulfide to give arsenic sulfide, As_2S_5, which is an indication that this acid also has slight basic action. The basic properties are very little pronounced.

phosphorus may be postulated. The hypothetical **antimonic acid** is a very weak acid, and has basic properties. As a result of its **acid properties,** the hydrated oxide dissolves in bases to form salts of the **meta**, the **ortho,** and the **pyro** type. Hydrochloric acid and hydrogen sulfide, on the other hand, react with hydrated antimony pentoxide to give $SbCl_5$ [1] and Sb_2S_5 respectively; the former remains in solution, the latter is precipitated. These reactions illustrate the **basic** properties of the pentoxide. Antimony trioxide probably combines to a slight extent with water to form antimony hydroxide (antimonous acid) which is **more basic than acidic.** It forms salts of the type $SbCl_3$ and Na_3SbO_3 (or $NaSbO_2$) illustrating both the basic and the acid ionization.

Bismuth pentoxide does not react with water. The bismuthates, derived from the hypothetical acid, $HBiO_3$, are unstable and little known. **Bismuth trioxide** has only **basic** properties forming salts of the $BiCl_3$ type.

In comparing the acids, the following **gradations in properties** are noted. In the first place, with increasing atomic weight the acids become less acidic and more basic. Also the hydroxide in which the element is trivalent is, in every instance, less acidic or more basic than the one in which it is pentavalent. In the second place, with increasing atomic weight, the acids in which the element is 5+ become less decided oxidizing agents, illustrating the increasing electropositive character of the elements. The only exception is found in the case of phosphoric acid which is so stable that it exhibits no oxidizing power whatever. Likewise, with the exception of the acids of phosphorus, the acids of the group become less stable with increasing atomic weight.[2] Finally, the tendency of the elements with higher atomic weight to take on an intermediate valence number, 3+, is shown by the decreasing reducing power of the **ous** acids and the increasing

[1] It is probable that the substance $HSbCl_6$ is formed by addition of HCl to $SbCl_5$ in solution.

[2] It is difficult to make an exact comparison because of the difference in state between the gaseous anhydrides of nitrogen and the solid anhydrides of the other acids. Likewise the uncertainty about the composition of the hydrated oxides of antimony and bismuth tends to cloud the situation. The statement made is unquestionably correct in a general way.

instability of the compounds in which the valence is 5+. The last point receives further illustration in the halogen compounds.

Phosphates and Analogous Salts of the Other Elements of the Group.—As has already been pointed out, orthophosphoric acid is tribasic, and therefore gives rise to one normal and two acid types of salts. The addition of 1 gram molecule of sodium hydroxide to 1 of phosphoric acid yields **primary** sodium phosphate, NaH_2PO_4, also called **mono-sodium phosphate.** Its aqueous solution is slightly acid because the $H_2PO_4^-$ ion is only slightly ionized into $HPO_4^=$ and H^+. Addition of another gram molecule of sodium hydroxide causes the formation of **secondary** or **di**-sodium phosphate, Na_2HPO_4. The last hydrogen of phosphoric acid, which still remains in this salt, is so slightly ionized that di-sodium phosphate is no longer acid in solution. In fact, the solution reacts alkaline towards indicators very sensitive to hydroxide ions because of hydrolysis according to the equation:

$$Na_2HPO_4 + H_2O \rightleftharpoons NaH_2PO_4 + NaOH \qquad (15)$$

The hydrolysis is, however, not very extensive; the salt does not redden phenolphthalein, which is not very sensitive towards bases but is sensitive to acids. Finally, the addition of a third gram molecule of sodium hydroxide converts the di-sodium phosphate into the **tertiary** or normal **sodium phosphate.** Since this salt is formed by neutralization of the very feebly ionized third hydrogen of phosphoric acid, it is very extensively hydrolyzed into the secondary phosphate and sodium hydroxide, and can be prepared in crystalline form only by using a large excess of the hydroxide. Its solution is strongly alkaline. The secondary phosphate is the one commonly used in the laboratory and is sold as sodium phosphate.

Equilibrium must exist between the primary, secondary and tertiary salts in solution, since the fundamental reaction underlying their formation from one another is completely reversible:

$$\begin{aligned} H_3PO_4 &\rightleftarrows H^+ + H_2PO_4^- \\ &\rightleftarrows H^+ + HPO_4^= \\ &\rightleftarrows H^+ + PO_4^{\equiv} \end{aligned} \qquad (16)$$

Consequently the removal of any of the products on the right drives the reaction in that direction. Thus, although only the first ionization is at all extensive, phosphate ions, $PO_4^{\equiv}$, can be formed in considerable quantity by adding an excess of a strong base which removes the hydrogen ion. On the other hand, the removal of phosphate ion must ultimately cause the complete ionization of the acid. In general the normal phosphates, except those of the alkali metals, are very slightly soluble, and consequently they, rather than the acid salts, are precipitated. Thus any orthophosphate gives the yellow, normal silver phosphate when treated with silver nitrate:

$$Na_2HPO_4 + 3AgNO_3 \rightleftharpoons Ag_3PO_4\downarrow + 2NaNO_3 + HNO_3 \quad (17)$$

Such phosphates are, however, dissolved by an excess of acid which converts them into the soluble primary or secondary salts.

Just as there is an equilibrium between primary, secondary, and tertiary phosphates, so equilibrium should exist between meta-, ortho- and pyrophosphoric acid. Since orthophosphates are generally less soluble than meta or pyro salts, precipitates of orthophosphates should be obtained from solutions of any one of the acids. This is actually the case if enough time is allowed for the attainment of equilibrium between the acids; but equilibrium is reached so slowly that meta- and pyrophosphates can be prepared. It is easier, however, to obtain them by heating acid orthophosphates. Primary phosphates yield metaphosphates:

$$NaH_2PO_4 \xrightarrow{\text{heat}} NaPO_3 + H_2O \quad (18)$$

and secondary phosphates [1] yield the pyro salts:

$$2Na_2HPO_4 \xrightarrow{\text{heat}} Na_4P_2O_7 + H_2O \quad (19)$$

In solution, the meta- and pyrophosphates are converted so slowly into one another that they may readily be detected. Thus metaphosphates give a white precipitate with silver nitrate and, when acidified, coagulate albumen. Pyrophosphates also give

[1] NH_4NaHPO_4, microcosmic salt, gives $NaPO_3$, and NH_4MgPO_4 gives $Mg_2P_2O_7$ on heating.

a white precipitate with silver nitrate, but do not coagulate albumen.[1]

The salts of arsenic and antimonic acids are like those of phosphoric acid. Since these acids are weaker than phosphoric, their salts are much more extensively hydrolyzed, and the normal salts more difficult to prepare unless they are very insoluble. The equilibrium between the meta, ortho and pyro forms is more rapidly established than in the case of the phosphoric acids. Thus potassium pyro-antimonate, $K_2H_2Sb_2O_7$,[2] is precipitated from solutions of antimonic acid because it is the least soluble of all of the possible antimonates of potassium.

Halogen Compounds of the Group.—All the elements of the group, except nitrogen, form **trihalides** with each of the halogens. Of nitrogen only the trichloride is known.[3] With the exception of nitrogen trichloride, all these compounds may be prepared by direct union of the elements. They illustrate once more the increase in the electropositive character of the elements with increase in atomic weight. Nitrogen trichloride is an explosively unstable compound; the others are very stable toward heat.[4] Nitrogen, phosphorus and arsenic trichlorides at ordinary temperatures are volatile liquids which are poor electrical conductors; in other words, they do not ionize extensively and are therefore not typical salts, as they should be if the elements in question were decidedly electropositive. Antimony trichloride is a solid melting at 73°. In the molten condition, it is a somewhat better conductor than the chlorides of phosphorus and arsenic. Bis-

[1] Pyro- and particularly metaphosphoric acid tend to form complex molecules in solution. Related to this fact is their tendency and that of their salts to form amorphous glassy masses instead of crystalline products when their solutions are evaporated to dryness. "Glacial phosphoric acid" is such a glassy, or "ice-like" metaphosphoric acid.

[2] Of the pyro acids, only salts in which either two or all four of the hydrogens are replaced are known. This is probably a matter of relative insolubility.

[3] See page 304.

[4] It has been suggested that the great difference in stability between nitrogen trichloride and the others is to be explained on the assumption that in this compound nitrogen is negative and chlorine positive, while in the others the chlorine is negative and the elements of the group are positive.

muth trichloride, a solid melting at 232°, is the most salt-like of the series in appearance, in conductivity in the molten condition, and in chemical reactions.

Nitrogen and phosphorus trichlorides are completely hydrolyzed by water even in the presence of excess of hydrochloric acid; arsenic trichloride may exist in solution if enough concentrated hydrochloric acid is present; antimony and bismuth trichloride are only partially hydrolyzed by water forming basic chlorides, as shown in the equation:

$$BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl \qquad (20)$$

The reaction is readily reversed by addition of an excess of hydrochloric acid.[1] True salts of strong acids like hydrochloric acid are not completely hydrolyzed; hence, nitrogen, phosphorus, and arsenic trichlorides are not, in this sense of the word, true salts.[2] In line with the behavior of the trichlorides of nitrogen, phosphorus and arsenic is the fact that these elements form neither nitrates nor sulfates, whereas antimony and bismuth do so.[3]

[1] It is easy to show why substances like SbOCl and BiOCl are called basic chlorides by writing equation (20) in steps. The first action of water on bismuth trichloride may be supposed to be:

$$BiCl_3 + H_2O \rightleftarrows Bi(OH)Cl_2 + HCl$$

$Bi(OH)Cl_2$ may be supposed to go over to BiOCl simply by the loss of 1 molecule of HCl. Another way of looking at the reaction is to suppose that the first step is:

$$BiCl_3 + 2H_2O \rightleftarrows Bi(OH)_2Cl + 2HCl$$

$Bi(OH)_2Cl$ might go over to BiOCl by loss of 1 molecule of water.

[2] Phosphorus pentachloride reacts with water to give the oxychloride $POCl_3$, which on further addition of water gives phosphoric acid. The reactions are, however, not reversible, and $POCl_3$ is an "acid chloride" rather than a basic salt of pentavalent phosphorus. (See page 271 for the definition of the term, acid chloride.)

[3] Another way of stating the same point of view is to say that the chlorides of the first three elements of the group are completely hydrolyzed because the substances $N(OH)_3$ (i.e., orthonitrous acid), $P(OH)_3$ and $As(OH)_3$ are such exceedingly weak bases that their salts are completely hydrolyzed, even though the acid (in this case hydrochloric) is very strong.

Phosphorus, arsenic and antimony form **pentafluorides**, phosphorus and antimony **pentachlorides** and **pentabromides**; no pentaiodides are known. Phosphorus pentachloride, PCl_5, is quite extensively used in organic chemistry, especially to replace hydroxyl groups by chlorine. The penta-halogen compounds are fairly readily decomposed by heat to yield the corresponding trihalide and free halogen. A number of compounds of the general formula $E_2(Hal)_4$, in which E represents an element of the group, are known.

The halogen compounds, especially those of phosphorus, are quite extensively used as reagents. Their hydrolysis, for example, constitutes a simple method of preparing both the corresponding halogen acid and the acid of phosphorus:

$$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr \qquad (21)$$

Details of the method are described on page 160. Their chief use, however, is in organic chemistry.

The Sulfides of the Group.—When sulfur acts on liquid ammonia, the substance **nitrogen sulfide**, N_4S_4, is obtained. It has, however, none of the characteristic properties of sulfides, and its nature is little known. Phosphorus forms a large number of sulfides, P_4S_3, P_4S_7, P_2S_5 and P_4S_{10}, all of which are obtained by heating phosphorus with sulfur in the proper proportions. They cannot be prepared by the action of hydrogen sulfide on phosphorus chlorides. Their character also is not thoroughly understood, but the series seems to represent a transition from the non-sulfide type of nitrogen sulfide to true sulfides. P_4S_3 is not readily attacked by the moisture of the air, and is non-poisonous; but it is readily inflammable by friction. For these reasons it has replaced the exceedingly poisonous white phosphorus in the **manufacture of matches.**

The sulfur compounds of arsenic, antimony and bismuth are typical sulfides. They are obtained either by direct union of the elements or by action of hydrogen sulfide on solutions of salts of the elements. The formation of the sulfides of arsenic has already been described in the discussion of the basic properties of arsenous and arsenic acids; the precipitation of bismuth sulfide from a bismuth salt is illustrated by the equation:

$$2Bi(NO_3)_3 + 3H_2S \rightarrow Bi_2S_3 + 6HNO_3 \qquad (22)$$

Arsenic and antimony form both tri- and pentasulfides; bismuth only the trisulfide.[1] One of the characteristics of the sulfides of arsenic and

[1] Arsenic also forms As_4S_3 and As_4S_4 which, in formula at least, are analogous to sulfides of nitrogen and of phosphorus.

antimony, important especially in analytical chemistry, is the fact that they are soluble in ammonium or sodium sulfide. The action of ammonium or sodium sulfide is a chemical one, resulting in the formation of the ammonium or sodium salts of the hypothetical **sulfo-acids**. The reactions in the case of arsenic may be represented by the equations:

$$3(NH_4)_2S + As_2S_3 \rightarrow 2(NH_4)_3AsS_3 \quad (23)$$

$$3(NH_4)_2S + As_2S_5 \rightarrow 2(NH_4)_3AsS_4 \quad (24)$$

The addition of the acid to the sulfo-salts (e.g., ammonium sulfarsenite) does not yield the free sulfo-acids (e.g., H_3AsS_3), for the latter at once decompose into hydrogen sulfide and the corresponding sulfides of arsenic or antimony. The ability to form salts of this type is not limited to arsenic and antimony. Tin, gold, platinum and, to a smaller extent, mercury behave in the same way. The reaction is used in analysis to separate those sulfides which dissolve in ammonium or sodium sulfide from those which do not.

The formation of the sulfo-acids is due to the union of the positive ions of arsenic or of antimony with sulfide ion to form the fairly stable compound ions $AsS_3^{\equiv}$, $AsS_4^{\equiv}$ $SbS_3^{\equiv}$ $SbS_4^{\equiv}$. The reaction is similar to the union of the positive ions of the elements with oxygen ion to form arsenite ion, $AsO_3^{\equiv}$, arsenate ion $AsO_4^{\equiv}$ etc. For this reason the sulfides which dissolve in ammonium sulfide (or in the sulfides of the alkali metals) are often spoken of as "acid forming sulfides" just as the oxides which react with bases are said to be "acid forming oxides."

EXERCISES

(1) Write the equations for the preparation of metallic bismuth from bismuth sulfide.

(2) Write the equations for the preparation of phosphorus by the old method. Balance those equations which represent oxidation and reduction by the electron method.

(3) Write equation (2) (page 391) in two steps which are analogous to the steps in the old method for making phosphorus. What rôle does the silicon dioxide play? What causes this reaction to go to completion?

(4) Why may white phosphorus be prepared only by rapid cooling of the vapor? Why does this form of phosphorus ordinarily have a yellow tinge?

(5) Explain the terms monotropic and allotropic. (See page 245.) Illustrate.

(6) Why are metastable modifications of a substance more active chemically than the stable forms of the same substance?

(7) Contrast the conditions under which nitrogen and the other elements of the group react with oxygen.

(8) (*a*) Suggest a method for the preparation of calcium phosphide. (*b*) Write the equation for the preparation of phosphine from calcium phosphide.

(9) Balance equation (4) (page 394) by the electron method.

(10) Phosphine reduces potassium permanganate, in the presence of sulfuric acid, to manganous sulfate. At the same time the phosphine is oxidized to phosphoric acid. Balance the equation by the electron method.

(11) In the action of zinc on arsenic acid, the latter is reduced to arsine and the former oxidized to zinc ion. Write the equation for the reaction, assuming that it takes place in sulfuric acid solution.

(12) Arsine reduces alkaline solutions of potassium permanganate to manganese dioxide. At the same time the arsine is oxidized to potassium arsenite. Assuming that potassium hydroxide is present, balance the equation.

(13) Make a comparison in tabular form of the hydrides of the elements of the nitrogen group. Point out how the similarities and differences can in most instances be predicted from the regularities generally found in outer groups of the periodic systems. Point out also the differences which are not encountered in other groups.

(14) Make a tabular comparison of the oxides of the group to bring out similarities and differences.

(15) (*a*) Why is phosphorus pentoxide a good drying agent? (*b*) What sort of gaseous substances might be dried by passing them over the pentoxide? (*c*) For what kinds must it not be used? (In answering the question consider the specific cases of NH_3 and HCl gas.)

(16) In what respects are phosphorus pentoxide and the corresponding acids exceptions to the regularities in the group?

(17) Give all of the illustrations you can of the fact that whenever an element forms more than one oxygen acid, the acid in which the element has the highest positive valence number is the strongest.

(18) Give all of the illustrations you can of the fact that the more electropositive an element, the more basic its hydroxide and the less acid its oxygen acids.

(19) Make a tabular comparison of the oxygen acids of the group. Do this in two sections, the one dealing with the acids in which the elements are trivalent, and the other with the acids in which the elements

are pentavalent. Make a brief statement to contrast the trivalent with the pentavalent types.

(20) Give examples showing that nitrous, phosphorous and arsenous acids are reducing agents.

(21) (*a*) What is meant by the statement that arsenous acid has basic properties? (*b*) Suggest a general method for determining whether a substance, which is either too insoluble or too slightly ionized to affect indicators decidedly, is an acid or a base.

(22) What are the formulae of the various types of salts of antimonic acid?

(23) Why are solutions of normal phosphates more extensively hydrolyzed than those of secondary phosphates, and these in turn more extensively than solutions of primary phosphates?

(24) What sort of acid would convert slightly soluble normal orthophosphates into primary phosphates, and what sort would completely (or nearly so) displace the phosphoric acid from the salt?

(25) In what respects do the gradations in properties of the chlorides in this group illustrate the increase in positiveness of the elements with increase in atomic weight?

(26) Explain why antimony oxychloride is called a basic salt.

(27) Collect all the facts which illustrate the tendency of elements of the group with higher atomic weight to take on a valence number intermediate between the highest and the lowest possible.

REFERENCES

Pring—The Electric Furnace (1921). Pages 343–346 describe the manufacture of phosphorus.

Rogers—Industrial Chemistry (1921). Pages 453–464 take up details of the phosphate rock industry.

Lowry—Inorganic Chemistry (1922). Chapters XXVII and XXXVI take up the elements of the group except nitrogen somewhat more fully than in this text.

CHAPTER XXVIII

CARBON

Distinctive Character of Carbon Compounds.—Groups in Organic Chemistry.—Structural Formulae.—Isomerism

Beginning with lithium, the elements in the first series of the periodic system become less and less electropositive with increasing atomic weight; from fluorine, on the other hand, with decreasing atomic weight, electronegative character becomes less pronounced. Carbon, which lies half way between the two extremes, should be very nearly as electronegative as electropositive. Such an element should exhibit properties quite decidedly different from those of most of the other elements. Everyone familiar with even the barest rudiments of chemistry must realize that this is actually the case. The hundreds of thousands of carbon compounds stand in marked contrast to the relatively small number which do not contain this element; the importance of carbon compounds in food and in the metabolism of all living beings illustrates the unique rôle which it plays; the dyes, the drugs, the explosives, textiles and plastics, most of which are carbon compounds, represent but a few examples that might be chosen to illustrate the vast importance of the element.

In the early days of scientific chemistry and biology it was generally believed that the carbon compounds produced by living organisms in the course of their life processes could not be prepared in other ways. A vital force, of somewhat mysterious character, was assumed to be essential in their formation. In consequence of this idea, these substances were called **organic compounds** to distinguish them from the inorganic ones, which seemed to possess no essential relationship to life. In 1828, however, Wöhler discovered quite accidentally that an inorganic substance, i.e., one which had been prepared in the laboratory,

could be converted into an organic one. He found that urea, $CO(NH_2)_2$, could be prepared by gently heating ammonium cyanate, NH_4OCN.

With this discovery, the old theoretical distinction between organic chemistry and inorganic disappeared. Since that time thousands of "organic" substances have been prepared without the intervention of life processes. Many of the dyes and drugs, which up to a few years ago were laboriously extracted from plants, are now expeditiously and cheaply manufactured in laboratories, and produced in a much purer condition than that in which they were ever found in nature. There is still, to be sure, a great deal to do. Biology awaits the developments of chemistry to show what is actually going on in living bodies. Many of the compounds most important to life are so complex that their structure is not yet known, and their manufacture is still to be accomplished. But each year the growing skill and knowledge of the chemist brings him closer to the desired end.

The division of chemistry into two groups, nevertheless, still possesses considerable advantage. In the first place, the chemistry of carbon compounds includes such a vast body of facts that specialization is required to permit of even partial mastery of them. In the second place, the reactions of carbon compounds generally differ in type from those of compounds of most other elements. Of course, no sharp distinction can be drawn, for the two types merge into one another, as has already been pointed out in another connection. But it may be broadly stated that the best examples of ionic reactions (i.e., of reactions between compounds believed to be formed by complete transfer of electrons) are found in compounds which are not essentially carbon compounds, whereas the best examples of reactions between compounds probably formed by electron sharing lie in the chemistry of carbon. For these reasons both the division and the names, inorganic and organic chemistry, have been retained. This chapter is not intended to be even an introduction to organic chemistry. Its purpose is to point out some of the characteristics which differentiate carbon from the other elements, the reasons for the multiplicity of carbon compounds, and the facts which make them the basis of life processes.

The Modifications of the Element.—Carbon exists in two definite modifications, diamond and graphite. Under readily realizable conditions, diamond is a metastable form, and goes over into graphite when transformation in measurable time is made possible by heat in the absence of air. Since diamond is more dense than graphite and since heat is given out when graphite is formed from diamond, rise of temperature and of pressure should favor the reverse action. But the density differences are not very large, and the amount of heat given out in the transformation is likewise small, so that very high temperatures and pressures are required to convert graphite into diamond. Small diamonds have actually been manufactured by applying these considerations. Iron saturated with carbon expands on cooling, while iron containing smaller amounts of carbon contracts. Moissan prepared a small cylinder of high carbon iron, with a carbon core. This he heated in a bath of molten low carbon iron. At the moment when the cylinder melted, the whole mass was rapidly chilled in water. The high carbon iron in the inner portion expanded while the outer portion contracted. Thus an enormous pressure was exerted on the carbon in the core, and diamonds were formed.

Other familiar forms of carbon are found in coke, charcoal, lamp black, and so on. They were formerly considered to be amorphous, i.e., supercooled liquid carbon, but recent examination by the X-ray method has shown them to consist of minute crystals of graphite, too small to be seen even through a microscope. It may be pointed out in this connection that the X-ray method has shown that the difference between diamond and graphite consists in a difference in arrangement of the carbon atoms—in diamond they are arranged so that any carbon atom lies equidistant from the four other nearest carbon atoms, while in graphite this is not the case.

Both forms of carbon are found in nature. Natural graphite constitutes the mineral plumbago. Graphite is also manufactured by heating the forms of carbon in which the crystals are submicroscopic to high temperatures for considerable periods. Apparently the small crystals grow to larger ones. Since graphite is very infusible and not very reactive, it is suitable for the

manufacture of crucibles. Because of its softness, it is used in pencils, and as a lubricant. It has very slight metallic conductivity, and is employed in units of high resistance, in telephones, and for electrodes in electrochemical work and arc lights.

Chemical Properties of Carbon.—As already mentioned, elementary carbon is not reactive. At ordinary temperatures, it combines with oxygen very slowly if at all, and then only if the carbon is very finely divided. At higher temperatures it reacts with oxygen or air to form carbon monoxide, if the supply of oxygen is limited, and carbon dioxide if sufficient oxygen is present. In these reactions a great deal of heat is liberated. The burning of substances or mixtures containing carbon (coal and wood) is at present the most widespread method of obtaining heat and power. At high temperatures carbon reduces oxides; illustrations are seen in the manufacture of many metals from their ores. When finely divided, carbon reacts with fluorine but not with the other halogens. On the other hand it may also react with electropositive elements. With hydrogen, at about 300° and in the presence of finely divided nickel acting as a catalyst, it gives methane. With metals it gives carbides. The formation of iron carbide, Fe_3C, is an important factor in steel making.

Carbon Dioxide.—Most of the important properties of carbon dioxide have already been discussed in various sections of this text, and in more elementary work. It may be frozen to a white solid by rapid expansion of the compressed gas. The solid is very volatile and usually sublimes, but may be melted under pressure at −56°. It is slightly soluble in water; one volume of the latter dissolves one volume of the gas at 15° and 760 mm. Water saturated at higher pressures with carbon dioxide is sold as soda water.

The reaction of carbon dioxide with water to form the weak, unstable **carbonic acid,** H_2CO_3, needs no detailed discussion. This acid, like all dibasic acids, forms normal and acid salts; acid carbonates are also called bicarbonates. Since it is a very weak acid, its normal salts, the carbonates, are hydrolyzed, and those of the alkali metals are strongly alkaline in aqueous solution; the bicarbonates, which are formed by neutralization of the first hydrogen ion only, are much less hydrolyzed. Thus the

bicarbonates of the alkali metals do not turn phenolphthalein red but are slightly alkaline toward methyl orange. Most of the normal carbonates are very little soluble in water; an exception is to be noted in the carbonates of the alkali metals. Carbonates may be converted into bicarbonates by the use of an excess of carbonic acid. For this reason calcium carbonate dissolves in water which contains carbon dioxide:

$$H_2O + CO_2 + CaCO_3 \rightarrow Ca(HCO_3)_2 \qquad (1)$$

Most acids displace carbonic acid from its salts. On this account carbonates and bicarbonates may be used to neutralize stronger acids. Bicarbonates are converted into carbonates by heat.

Carbon Monoxide.—Carbon monoxide is prepared in the laboratory by heating sodium formate, HCOONA, with concentrated sulfuric acid. The latter removes water from the formic acid which is probably first formed:

$$HCOOH \rightarrow CO + H_2O \qquad (2)$$

On the large scale it is produced either by blowing air through burning coke or by passing steam over white hot coke. In the former reaction a mixture of nitrogen and carbon monoxide, containing about 40 per cent of the latter, is obtained. It is known as **producer gas.** The action of water results in the formation of carbon monoxide and hydrogen:

$$C + H_2O \rightarrow CO + H_2 \qquad (3)$$

The mixture of the two gases is called **water gas.** From it illuminating gas is manufactured by the admixture of small amounts of volatile hydrocarbons. In the reaction between carbon and hydrogen, heat is absorbed, and the mixture must therefore be heated to maintain the action. This is accomplished by blowing air and steam alternately through the coke. Water gas and producer gas are used industrially as fuel gases; the former is employed largely also for cooking and domestic heating. From water gas, hydrogen may be prepared commercially. If an excess of water is added to it and the mixture passes over a catalyst such as iron oxide, the following reaction occurs:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (4)$$

The hydrogen may be freed from carbon dioxide by first washing the gas with water under pressure and then removing the residual carbon dioxide with lime.

Properties of Carbon Monoxide.—Carbon monoxide is an odorless, colorless gas. The boiling point of the liquid is $-190°$. It is very slightly soluble in water. It is a reducing agent at high temperatures, and is used to convert oxides into free metals. In the presence of catalysts or of sunlight, it reacts with chlorine to form phosgene, $COCl_2$, which was used as a war gas. It unites with iron and nickel to form the curious compounds called carbonyls, of which nickel carbonyl, $Ni(CO)_4$, is an illustration.

Carbon monoxide is very poisonous. One part in about 100,000 of air produces illness, and one part in about 750 of air leads to death in a short time. The carbon monoxide combines with the haemoglobin of the blood corpuscles, and thus prevents their taking up oxygen. By the breathing of pure air, the carbon monoxide may again be removed from the blood. Since the gas is produced by incomplete combustion of carbon compounds (such as occurs in automobile cylinders) and is a component of illuminating gas, many deaths have resulted from poisoning by it.

Other " inorganic " Carbon Compounds.—Without any fundamental reason for making the distinction, certain carbon compounds such as the oxides, the sulfide and a few others are called inorganic. **Carbon disulfide,** prepared by the union of sulfur vapor and glowing carbon, is used chiefly as a solvent. The same is true of carbon **tetrachloride,** which is manufactured according to the reaction:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2 \qquad (5)$$

A familiar illustration of its solvent action is its use as a cleaning fluid (carbona). It is used also in fire extinguishers. When the liquid is blown into the fire,[1] it evaporates and displaces the air. At the same time the heat of evaporation cools the burning

[1] The use of carbon tetrachloride as a fire extinguisher may result in the formation of the very poisonous phosgene, $COCl_2$. Rooms in which this material has been used to extinguish a blaze must be thoroughly ventilated at once.

mass. The carbon tetrachloride itself cannot burn because its carbon has the valence number 4+, and thus is already oxidized as completely as possible.

Carborundum is a compound of silicon and carbon, obtained in the electric furnace by the reaction:

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (6)$$

The product, which is very hard, is molded into grinding wheels. It is largely displacing emery. **Calcium carbide,** also an electric furnace product ($3C + CaO \rightarrow CaC_2 + CO$), is the most common source of acetylene, which is obtained by treating the carbide with water:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \qquad (7)$$

The use of calcium carbide in the manufacture of cyanamide has already been mentioned (page 298).

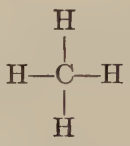
Hydrocyanic acid, or **prussic acid,** and its salts, the **cyanides,** are important reagents. They are very poisonous and are used as insect exterminators, particularly on fruit trees; they are powerful reducing agents, hence they are used in metallurgy and other chemical processes. They have a great tendency to form compounds containing complex cyanide ions. This property leads to their use in analytical chemistry and in metallurgy for the extraction of gold. Illustrations of their ability to form these complexes will be given in later chapters. **Cyanogen** (C_2N_2), formed by direct union of the elements in the electric arc and obtained by decomposition of cyanides, is of considerable theoretical interest but need not be discussed here. Like hydrocyanic acid, cyanogen is very poisonous.

In carbon dioxide, the tetrachloride and the sulfide, carbon may be looked upon as having the valence number 4+. None of these compounds shows by its behavior even a trace of ionization into a quadrivalent positive carbon ion. It is therefore likely that the bond which holds the atoms together is due to sharing of electrons rather than to complete transfer of electrons from carbon to the other element. Nevertheless, many chemists are of the opinion that the behavior of these compounds is best explained by assuming partial polarity, such as would exist if the

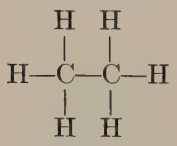
pairs of shared electrons lay closer to the oxygen, the chlorine or the sulfur atoms—in other words that carbon in these compounds is slightly more positive than the other elements. (See pages 366–367.)

The Hydrocarbons.—Carbon and hydrogen form a very great number of compounds which contain these two elements only. The substances are called hydrocarbons.

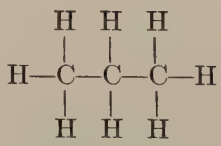
The Paraffine or Saturated Hydrocarbons.—The simplest compound of hydrogen and carbon is methane. In it, 4 hydrogen atoms are bound to a carbon atom as illustrated by the formula:



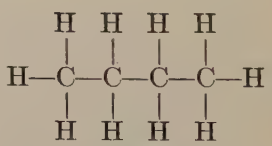
The lines drawn between the carbon atom and each of the hydrogens indicate how the atoms are arranged in the molecule. In writing such a **structural formula** it is not necessary to make any assumptions with regard to the nature of the bond which holds the atoms together. However, in these hydrocarbons the bond is probably due to the sharing of electron pairs. There are other compounds very similar to methane in all of their reactions; only a few of the simpler ones need be mentioned: ethane, C_2H_6, propane, C_3H_8, and butane, C_4H_{10}. The formulae as given, tell only the relative numbers of atoms in the molecule and the molecular weight; these are the **empirical formulae,** derived simply from analytical data and molecular weight determinations. But the structural formulae for these compounds are also known:



ethane



propane



butane

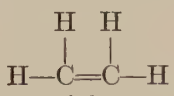
In a later paragraph the type of reasoning by which structural formulae are arrived at, is briefly outlined.

The striking fact illustrated is that carbon may be joined to carbon to form **long chains** which are, so to speak, the backbones of the carbon compounds. In this fact lies one of the reasons for the great number of substances containing carbon. A second point of importance is that in all of the hydrocarbons mentioned, each of the atoms is bound by **single bonds**; in terms of the Lewis hypothesis, each of the atoms shares with other atoms only single pairs of electrons. This assumption is based on the fact that these hydrocarbons are unable to take up chlorine or bromine or hydrogen as do other types to be discussed in the next section. For this reason the compounds are called the **saturated hydrocarbons.** The name, **paraffine hydrocarbons,** is also used because some of the natural products known as paraffines are hydrocarbons of this type. Each of the end carbons has 3 hydrogens attached to it, while each of the carbons in the middle of the chains has only 2. For this reason the empirical formulae of the saturated hydrocarbons may be given in the generalized form, C_nH_{2n+2}.

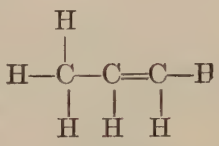
The saturated hydrocarbons are chemically very inert. When heated in air they burn, giving carbon dioxide and water, if the temperature is sufficiently high and the oxygen supply ample, or mixtures containing water and free carbon at lower temperatures or in a limited supply of oxygen. Burning is probably preceded in all cases by dissociation of the hydrocarbons, for all of them are relatively unstable, even though their decomposition at lower temperatures may be very slow. Methane, the most stable of the group, is partially dissociated at 300°; decomposition is favored by rise in temperature. Many of the hydrocarbons are apparently metastable substances even at ordinary temperatures, although at present the data are insufficient for definite conclusions with regard to most of them. They react with chlorine by substitution in the presence of catalysts; more vigorously with fluorine and less so with the other halogens. In general, the hydrocarbons containing the larger numbers of carbon atoms are the less reactive ones.

Unsaturated Hydrocarbons. Olefines and Acetylenes.—The **olefines** are compounds containing a pair of carbon atoms which may be considered to be bound by a double bond, that is by the

sharing of two pairs of electrons.[1] Illustrations of this type are found in ethylene, C_2H_4, and propylene, C_3H_6, for which the structural formulae are:



ethylene



propylene

The generalized olefine formula for hydrocarbons is C_nH_{2n}. Still another type of hydrocarbons contains a pair of carbon atoms joined by triple bonds; these compounds are called **acetylenes.** The simplest one is acetylene:

$$H—C\equiv C—H$$

Olefines and acetylenes are **unsaturated** hydrocarbons. The idea of double and triple bonds has been devised by chemists to interpret differences in chemical behavior like those between the paraffines and the unsaturated hydrocarbons. The latter are capable of adding hydrogen, especially in the presence of catalytic agents. Thus propylene in the presence of platinum black gives propane:

$$C_3H_6 + H_2 \rightarrow C_3H_8 \qquad (8)$$

It may be mentioned that the hardening of certain vegetable oils to convert them into fats for use in cooking is a process of this sort. In similar fashion the unsaturated hydrocarbons add chlorine and bromine, halogen acids and sulfuric acid. Compounds which contain one double bond add on only 1 molecule of hydrogen or of chlorine, while those containing one triple bond are capable of adding 2 molecules.

The **formation** of the **olefines** and **acetylenes** cannot be taken up in detail. It may be mentioned that methane is decomposed by heat into ethylene, acetylene and hydrogen:

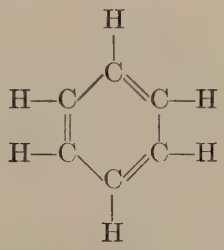
$$2CH_4 \rightarrow C_2H_4 + 2H_2 \qquad (9a)$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \qquad (9b)$$

[1] Compounds with more than one double bond are known as poly-olefines.

When hydrocarbons of high molecular weight are used, lighter hydrocarbons result. Such reactions are illustrations of the process known as "cracking" hydrocarbons. The process has important technical application in converting the heavier, less reactive hydrocarbons into the lighter ones, which may be used as fuel for automobile and other internal combustion engines. The manufacture of acetylene from calcium carbide has already been mentioned.

Hydrocarbons of the Aromatic Series.—In addition to forming compounds by uniting in chains of single, double and triple bonds, carbon also unites with itself in **closed chains** or **rings.** Although a detailed study of this subject would lead too far afield, the substance **benzene** (sometimes incorrectly called benzol) is too important an illustration of this important class of substances to be entirely omitted. Its empirical formula is C_6H_6; the structural formula usually assigned is:



This formula represents a vast amount of experimental work which cannot be recounted here. Compounds containing rings of carbons like that of the benzene molecule are called **aromatic** compounds, since many of the aromatic essences extracted from plants belong to this group. Their properties and uses are so important that a special branch of organic chemistry is devoted to them. Among the aromatic compounds are dyes, drugs, high explosives and so on.

Occurrence of Hydrocarbons.—The most important source of hydrocarbons of the paraffine series is petroleum. American petroleum consists largely of members of the paraffine group. By fractional distillation the more volatile components are separated from the less volatile ones. The first fraction con-

sists chiefly of pentane and hexane (C_5H_{12} and C_6H_{14}). It is used as a solvent, and in supplying hydrocarbons to fuel gas in order to convert it into illuminating gas. The next fraction is gasoline, a mixture of various hydrocarbons of which hexane and heptane (C_7H_{16}) are the most important. The heavier fractions are sold as naphtha, benzine, and kerosene. Still heavier fractions are vaseline and solid paraffines. Asphalt is a mixture of high boiling solid hydrocarbons. The olefines also are found to some extent in natural oil and some of them are formed during the process of distilling the latter. Hydrocarbons of the benzene type are obtained from coal tar—one product of the destructive distillation of coal carried out in the manufacture of coke.[1]

Halogen Derivatives of the Hydrocarbons.—Chlorine, in the presence of a suitable catalyst or under the influence of light, reacts by substitution with saturated hydrocarbons, especially with those of lower molecular weight. The difference in the behavior of the unsaturated and saturated hydrocarbons is illustrated by writing the equations for the reactions of ethylene with bromine and of methane with chlorine:

$$H_2C{=}CH_2 + Br_2 \rightarrow \underset{\text{ethylene dibromide}}{H_2BrC{-}CBrH_2} \qquad (10)$$

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \qquad (11)$$

In the latter case the reaction does not necessarily stop when chlorine has been substituted for one of the hydrogens but dichlormethane, CH_2Cl_2, chloroform, $CHCl_3$, and carbon tetrachloride, CCl_4, are formed in addition to the methyl chloride, CH_3Cl shown in the equation. (See page 157.) Similar reactions occur with other saturated hydrocarbons. The halogen derivatives, although called **alkyl halides,** are not salts; they are not conductors either in the pure condition or in solution, they do not display the abnormally low molecular weights characteristic of dissociation, nor do they react rapidly by double decomposition.

Alcohols.—Action of water or of weak bases on alkyl chlorides or other halides converts them more or less completely into compounds in which an OH group has taken the place of the halo-

[1] See page 296.

gen. Thus the resulting **alcohol** may be looked upon as formed from a hydrocarbon by substituting an OH group for one of the hydrogens. Familiar illustrations are methyl or wood alcohol, CH_3OH, and ethyl or ordinary alcohol, C_2H_5OH. The **hydroxyl group,** OH, must be distinguished from the hydroxide ion, OH^-. Alcohols are not bases. As a matter of fact their slight ionization shows them to be acids although exceedingly weak ones. They react only with the most active metals such as sodium or calcium, and but slowly even with these.

Aldehydes, Ketones, and Sugars.—Oxidation of alcohols by mild oxidizing agents may lead to the formation of **aldehydes** or of **ketones.** The former may be looked upon as compounds containing the $-\overset{H}{\underset{|}{C}}=O$ group; for example, the formula of formaldehyde is $H-\overset{H}{\underset{|}{C}}=O$, that of acetaldehyde, $CH_3\overset{H}{\underset{|}{C}}=O$. Aldehydes possess a large number of characteristic reactions among which is their marked reducing power. Thus they react with Fehling's solution to precipitate red, hydrated cuprous oxide (see page 515). Ketones contain the carbonyl group, $=C=O$, as in dimethyl ketone (acetone) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=O$. Neither type of compound is extensively used in inorganic reactions, but both are of great importance in organic chemistry. They are mentioned here chiefly to illustrate the fact that organic compounds often belong to more than one type. Thus many sugars are both alcohols and aldehydes. The formula of glucose, for example, may be written

$$\begin{matrix}H & H & H & H & H & H\\ | & | & | & | & | & |\\ H-C-C-C-C-C-C=O\\ | & | & | & | & |\\ O & O & O & O & O\\ H & H & H & H & H\end{matrix}$$

The first 5 carbon atoms are attached to other carbon atoms and to hydrogen and hydroxyl groups, and these combinations there-

fore constitute alcohol groups; while hydrogen and oxygen are attached to the last carbon as in an aldehyde. Like other aldehydes, glucose reduces Fehling's solution, and at the same time possesses many of the properties of typical alcohols. Cane sugar, although possessing properties of an alcohol, does not reduce Fehling's solution. It therefore does not contain the aldehyde group. But if boiled for a short time with acids it is converted into two compounds one of which is of the aldehyde type. The reaction which occurs is represented by the equation:

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \qquad (12)$$

Glucose and fructose differ somewhat in properties from one another, although they have the same empirical formula. They are isomers, a term which will be explained in a later section of this chapter. There are other sugars besides these two which also have the same formula. To all of them the group name, **monosaccharides,** has been given. Cane sugar is one of several **disaccharides.** Starch $(C_6H_{10}O_5)_x$ and cellulose $(C_6H_{10}O_5)_y$ are closely related to the sugars. The general name, **carbohydrate,** is used for all of these compounds since all of them contain hydrogen and oxygen in the proportions in which they occur in water.

Organic Acids.—Oxidation of aldehydes or of alcohols by moderately strong oxidizing agents leads to the formation of organic acids, substances which contain the carboxyl, $-C\overset{OH}{\diagdown}=O$, group. There are a great number of compounds belonging to this class. Of these, formic acid, $HC\overset{OH}{\diagdown}=O$, acetic acid, $H-\underset{H}{\overset{H}{C}}-C\overset{OH}{\diagdown}=O$, and oxalic acid, $\begin{vmatrix} C\overset{OH}{\diagdown}=O \\ C\diagup\!\!=O \\ \quad OH \end{vmatrix}$, may be mentioned. Formic acid is the simplest organic acid, acetic acid has been frequently encountered elsewhere in this text, and oxalic acid is extensively used in inorganic chemistry. It is a good reducing

agent; in the reaction it is oxidized to carbon dioxide and water, as shown in the equation:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \rightarrow 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O \quad (13)$$

It is also used in qualitative analysis because it precipitates certain ions as insoluble oxalates. In industry it is used as a bleach, and in other ways.

A very convenient and useful classification of carbon compounds is based on the fact, illustrated in the preceding paragraph, that the presence of certain groups in organic compounds imparts definite chemical properties to them. The subject of organic chemistry may therefore be presented in part as a study of the properties due to the various important groups, just as in analytical chemistry emphasis is placed on the reactions of the various ions. But it must be remembered that these groups are not ionized. They do not exist in solutions as practically independent units, and the presence of one group in a compound often affects the properties of the other groups.

Esters.—Alcohols react with organic acids to form esters, as illustrated by the equation:

$$\underset{\substack{\text{ethyl}\\\text{alcohol}}}{C_2H_5OH} + \underset{\substack{\text{acetic}\\\text{acid}}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH} \rightarrow \underset{\substack{\text{ethyl ester}\\\text{of acetic acid}\,[1]}}{C_2H_5{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + H_2O \quad (14)$$

This equation bears a superficial similarity to one representing the formation of a salt by interaction of an acid and a base. In reality the two types of reaction are entirely different. Esters are not salts, for they are completely un-ionized, and alcohols are not bases. In contrast to typical ionic reactions, ester formation is usually a relatively slow process. The reactions are reversible. The interaction of an acid and an alcohol to form water and an ester is called **esterification**; the reverse action is called **saponification** of the ester.[2]

[1] This substance is also called ethyl acetate.

[2] The term hydrolysis, sometimes used for the action of water on an ester, is reserved in this text for the typically ionic reaction between water and a salt.

Among the esters are some compounds of great everyday importance. When ordinary fats are heated with solutions of sodium hydroxide or of some other similar substance, glycerine and soaps are obtained. **Glycerine**, $H_2C(OH)-C(H)(OH)-CH_2(OH)$, is an alcohol which contains three alcohol groups. The **soaps** are salts of organic acids which contain long carbon chains. **Palmitic,** $C_{15}H_{31}COOH$, **oleic,** $C_{17}H_{33}COOH$, and **stearic acid,** $C_{17}H_{35}COOH$, are the acids most commonly involved. The formation of glycerine and soaps in these reactions demonstrates that the **fats are esters** in which the 3 hydroxyl groups of the glycerine have been esterified by 3 molecules of these acids,[1] and that soap formation is a process of saponifying these esters. The sodium salts of these long chain organic acids are "hard soaps," and the potassium salts "soft soaps." Their function in cleansing will be discussed in the next chapter.

Ethers.—Ethers are compounds in which an oxygen atom takes the place of 2 hydrogens from two different molecules of a hydrocarbon. Thus dimethyl ether, CH_3OCH_3, consists of two CH_3 groups joined by an oxygen atom. Diethyl ether, the anaesthetic, is $C_2H_5OC_2H_5$. Towards most reagents, ethers are relatively inert. They do not act, as do alcohols, with even the most active metals, nor do they form esters with acids. They are not readily decomposed by water or alkalies.

Determination of Structural Formulae.—The determination of structural formulae is a very important problem, which for compounds containing many atoms, may be very difficult to solve. Thus the structure of indigo was elucidated only after years of patient and brilliant research; but the successful solution of the problem soon resulted in a method of preparing the dye artificially at less expense and in purer condition than it

[1] It is not necessary that the three hydroxyl groups are all esterified by the same one of the acids. The more common fats, in fact, are esters of more than one of the acids with the same glycerine molecule, and the soaps formed from them are therefore mixtures.

could be obtained from natural sources. The experimental methods and reasoning by which structures are determined are illustrated in the following relatively simple case.

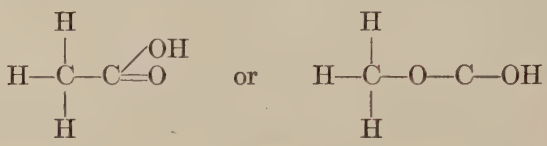
Analyses and molecular weight determinations of acetic acid lead to the empirical formula $C_2H_4O_2$. To neutralize completely 1 gram molecule of the substance only 1 gram molecule of sodium hydroxide is required; likewise 1 gram molecule of acetic acid reacts with but 1 gram atomic weight of sodium to liberate 1.008 grams of hydrogen. These experiments show that only one of the 4 hydrogen atoms of the molecule is ionizable. Furthermore, treatment of the substance with phosphorus pentachloride leads to the formation of the substance C_2H_3OCl. Evidently 1 hydrogen and 1 oxygen have been removed from the molecule by the action of the pentachloride. The compound C_2H_3OCl contains no ionizable hydrogen; hence, the ionizable hydrogen of acetic acid must have been attached to oxygen. This conclusion is borne out by the fact that the acid chloride, C_2H_3OCl, again gives acetic acid by treatment with water:

$$C_2H_3OCl + H_2O \rightarrow C_2H_3OOH + HCl$$

The experiments just described prove that the ionizable hydrogen is attached to one of the oxygens of acetic acid. Reduction of acetic acid leads to the formation of ethyl alcohol, C_2H_6O. But the alcohol also contains the OH group, as is shown by its reaction with phosphorus pentachloride, in which the oxygen and 1 hydrogen are both replaced by 1 chlorine, Hence, ethyl alcohol must be CH_3CH_2OH. Since the OH group of the alcohol is attached to carbon, the same must be true of the OH group of acetic acid from which the alcohol was prepared.

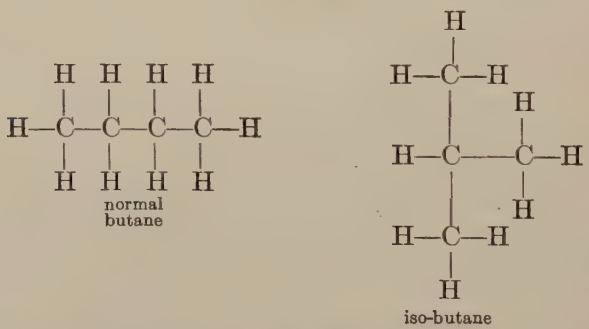
Finally, acetic acid reacts with chlorine to give $C_2HO_2Cl_3$. This substance still is an acid, and its behavior shows that the OH group which furnished the hydrogen ion in acetic acid is still present. Furthermore, the replacement of hydrogen by chlorine is a characteristic reaction of hydrocarbons, that is, of substances containing hydrogen bound to carbon. Hence,

3 of the hydrogens of acetic acid must be bound directly to carbon. Only two possible structures are now left to chose from:



The second of these is an unsaturated compound, for only 2 of the 4 valences of the second carbon are satisfied. But acetic acid has none of the properties of that kind of compound; consequently the first formula is correct, and the second wrong.

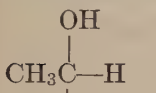
Isomerism.—There is one other factor which contributes to the multiplicity of carbon compounds and is of both great theoretical and practical interest. An examination of the structural formula of butane reveals the possibility of two different arrangements of the carbon and hydrogen atoms:



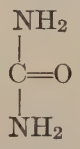
Actually two substances of the empirical formula C_4H_{10} are known. The one with properties best explained by assuming that all of the carbons lie in a single straight chain is called **normal butane.** It boils at approximately $+1°$. The one which, to account for its properties, is formulated as having a branched chain, boils at $-17°$ and is called iso-butane. The larger the number of atoms, the greater the number of possible arrangements of the same atoms within the molecule.

Substances which have the same empirical formula (that is the same number and kind of atoms in the molecules) but which

differ because of differences in arrangements are called **isomers.** Another interesting illustration is the case of dimethyl ether and ethyl alcohol, both of which have the empirical formula C_2H_6O. The former at ordinary temperatures is a gas which does not react with sodium or with organic acids; ethyl alcohol is a liquid which reacts with acids to give esters, and with metals such as sodium to give hydrogen. In accordance with these facts the structural formula $H_3C—O—CH_3$ is assigned to the ether, and



to the alcohol. Urea and ammonium cyanate are another pair of isomers. The former is



while the latter is $(NH_4)OCN$. Other types of isomerism which depend upon **differences in spacial arrangement** (**stereoisomerism**) rather than upon differences in the ways in which the atoms are attached to each other, cannot be discussed in this text.

It is obvious that isomerism greatly increases the number of possible compounds and the complexity of organic chemistry. A large number of interesting facts is connected with the function of isomers in nature. Animals and plants may produce or utilize as food but one of two substances which differ from each other only in the spacial arrangement of the atoms. Separation of isomers by bacterial action is sometimes possible for this reason.

The Justification for Structural Formulae.—Structural formulae represent the way in which the atoms are believed by chemists to be attached to each other.[1] It is quite possible that in many instances the picture is incomplete, and that in others it may depart quite widely from the truth. X-ray analysis of crystals of organic compounds is a possible method for determining the actual structural relations with more precision. Neverthe-

[1] It must be understood that the structures really represent the atoms arranged in three dimensions rather than in two. The plane formulae commonly used are convenient projections.

less chemists have a great deal of confidence that the structural formulae are at least quite close to the truth in most cases. From these formulae, they have not only been able to predict the existence of isomers but also to forecast their exact numbers, and in practically all cases investigated the predictions have been verified. But in addition to this, structural formulae are important because they summarize the chemical behavior of the substances which they represent.

Résumé of the Properties of Carbon and of its Compounds.—The outstanding characteristics of the chemistry of carbon have been briefly outlined in the preceding pages. In accordance with the position of the element in the middle of the first series of the periodic system, it is neither decidedly electropositive nor electronegative, and free carbon ion does not exist. Although it forms ionized compounds such as the organic acids and their salts, the characteristic reactions of carbon compounds are non-ionic. Carbon probably forms compounds by electron sharing both with electropositive and electronegative elements. Furthermore, its atoms may be joined to each other in long chains or rings. This fact leads to the existence of isomers and of large numbers of compounds. The chemical reactions of many carbon compounds are relatively slow, but may be hastened by catalytic agents. For all of these reasons the chemistry of carbon is extremely diversified.

The Function of Carbon Compounds in Life.—Life as it is found on the earth is distributed among many species some of which are highly complex. Different living beings, and the various parts of the more complex animals and plants, perform widely different functions. Since most of the functions of life are carried on through chemical reactions, it is obvious that a great variety of chemical substances is necessary. The necessary compounds must also possess a certain stability (especially toward water and oxygen) if life based on them is to be possible. On the other hand, substances which constitute the bodies of living organisms must be reactive in order to fulfill their vital functions. This explains the importance of the fact that many carbon compounds, although ordinarily extremely slow to react, can react more rapidly in the presence of catalysts. In the living

body the catalysts are the substances called enzymes, such as pepsin or trypsin, and the glandular extracts, such as adrenalin or insulin. Finally, the energy required for life is obtained by the burning of carbon compounds to carbon dioxide. The latter is a gas which is readily eliminated and diffuses throughout the atmosphere; it is somewhat soluble in water, and is therefore carried from place to place in solution; under the influence of light and the action of chlorophyll it is reconverted by plants into compounds which animals use for food. Thus the carbon, burned in the body, is not lost but enters into what is called a life cycle.

Other Carbon Compounds.—The preceding discussion of some of the characteristics of carbon chemistry has been limited to compounds containing only carbon, hydrogen and oxygen merely to make it as simple as possible. Practically all of the elements may be constituents of organic compounds. Compounds containing nitrogen are very numerous and of great importance. Aniline and the aniline dyes, trinitrotoluene (the high explosive), drugs such as phenacetin are but a few examples. The most important nitrogenous compounds are the proteins. Organic sulfur compounds are also important in living organisms and in industry; arsenic and mercury compounds are used in medicine. It is not intended, however, to give here a list of the organic compounds of all of the elements, but merely to make clear that the limitation put on the discussion in this text is only one of convenience.

EXERCISES

(1) Explain the origin of the term "organic" chemistry. Why is the term no longer applicable in its original sense?

(2) What are the two forms of carbon and under what conditions may they be transformed into each other?

(3) What are the reasons for the statement that carbon appears to have a greater tendency to be electropositive than electronegative, if it is either?

(4) Explain why carbon dioxide gas solidifies when it is suddenly expanded from a highly compressed condition.

(5) Assuming that Henry's law is applicable, calculate the solubility of carbon dioxide at 15° and 4 atmospheres pressure.

(6) Name three facts which show that carbonic acid is a weak acid.

(7) Why are carbonates more extensively hydrolyzed than bicarbonates?

(8) Explain why calcium carbonate dissolves when an excess of carbon dioxide is passed through a suspension of the carbonate in water.

(9) Why are carbonates used to neutralize strong acids?

(10) Name the important properties of carbon monoxide.

(11) (*a*) What experimental facts are implied in the statement that carbon dioxide, carbon tetrachloride and carbon bisulfide do not show a trace of ionization? (*b*) How are the elements in these compounds believed to be bound?

(12) (*a*) Define the terms "saturated hydrocarbon" and "unsaturated hydrocarbon." (*b*) What experimental differences in the behavior of the two classes are implied in the terms?

(13) (*a*) What is a structural formula? (*b*) Show by means of an illustration how structural formulae are used to indicate the chemical properties of the corresponding substances.

(14) Suggest a method of determining how many double bonds there are in a hydrocarbon (see page 420).

(15) (*a*) Write the equation for the preparation of ethyl alcohol from ethyl chloride. (*b*) What is the ordinary method of manufacturing alcohol?

(16) Write the formulae of the characteristic groups of the following classes of compounds: alcohols, esters, organic acids, aldehydes, ethers.

(17) Explain the difference between the action of an alcohol and of a base on an organic acid.

(18) Define the terms "saponification" and "esterification."

(19) What are (*a*) fats? (*b*) soaps?

(20) (*a*) What is meant by "isomerism"? (*b*) Give two illustrations. (*c*) How many isomers could there be corresponding to the formula C_5H_{12}?

(21) (*a*) What are the outstanding differences between carbon compounds and those of the other elements? In what way do these differences agree with the position of carbon in the periodic system?

(22) Give the reasons for the importance of carbon compounds to living organisms.

REFERENCES

Lowry—Inorganic Chemistry (1922). Chapter XXVIII, in addition to describing carbon and many of its compounds briefly, gives information about fuels.

Moissan—The Electric Furnace (translated by Lenher). The book contains descriptions of various models of electric furnaces devised by Moissan and the types of experiments first carried out with them. The preparation of the different forms of carbon, including diamond, is described in some detail. The preparation of many metals and their carbides is also taken up. For the details of modern electric furnaces, especially as used in industry, the reader is referred to

Pring—The Electric Furnace (1921) which, in addition to historical material and the details of furnace construction, takes up graphite, pages 336–343, calcium carbide, pages 102–114, and carborundum, pages 326–334. Other phases of electric furnace practice are of course also discussed.

Organic chemistry is so large a field that references could be given only to elementary texts on the subject, which would be too extensive for collateral reading. Descriptive material about organic compounds is contained in many text books of general chemistry. For example

Smith's College Chemistry, revised by J. Kendall (1923). Chapters XXXVI, XXXVII, XXXVIII, XXXIX and XLII.

McCoy and Terry—Introduction to General Chemistry (1920). Chapters XXV and XXVI.

Applications of organic chemistry to industry are entertainingly described in most of the chapters of

Slosson—Creative Chemistry (1921). Even to one familiar with the book, rereading those chapters particularly devoted to carbon chemistry will be of value, if the notions of structure developed in this chapter of the text are applied to them.

Many of the chapters in Rogers, Manual of Industrial Chemistry, deal with organic compounds. For example: Chapter XX, Illuminating Gas, Chapter XXI, Coal Tar and Its Distillation Products, Chapter XXII, The Petroleum Industry.

CHAPTER XXIX

THE COLLOIDAL CONDITION

Osmotic Pressure

Between coarse suspensions and true solutions there exists an intermediate type of mixture which has some of the properties of ordinary mixtures and some of those of solutions. A hard lump of clay dropped into a pail of water falls rapidly to the bottom. But if the lump is broken up by grinding it into much smaller grains, the rate of settling becomes much slower. As the size of the particles is diminished the surface of the whole quantity of suspended material, upon which friction is developed, becomes larger. If the process of grinding is continued, the size of the particles becomes constantly smaller and the rate of settling correspondingly slower.

A second factor also comes into play to prevent settling. A suspended particle is continuously bombarded by the rapidly moving solvent molecules. As long as the particle is large, this bombardment has little influence, since the number of molecules striking on a large area from above is equal to the number striking from below. But when the area of the suspended particle becomes so small that it is not more than, let us say, a hundred or a thousand times the area of a solvent molecule, the number of impacts from different directions is no longer necessarily the same at all times. Moreover not all the solvent molecules move with the same velocity. In the case of a suspended particle with area of the same order of magnitude as that of the solvent molecules, more of the fast-moving molecules may, at a given moment, strike the suspended particle from one direction than from another. At one instant the larger number of fast-moving molecules may strike from above; at the next moment they may strike from one side. As a result, irregular motions, already described as the **Brownian**

Movement (pages 46–47), are imparted to the suspended grains, and settling is prevented.

Permanent suspensions of this sort are called **colloidal** suspensions or **colloidal** emulsions. The term colloidal solutions is often used, especially for the emulsion type of colloidal mixtures. A better system of terminology designates the colloidal mixture as a **dispersed system,** the suspended material as the **dispersed phase,** and the substance in which dispersion takes place as the **dispersing medium.** It is obvious that the latter term is far better than the term " solvent " because dispersed systems are not true solutions.[1]

Types of Colloidal Mixtures.—The most varied types of colloidal mixtures are possible. Liquids or solids may be dispersed in gases, as in fog or in smoke; gases may be dispersed in liquids to produce foams, or in solids to produce mixtures like pumice. Liquids dispersed in other liquids form emulsions; when they are dispersed in solids, they produce rigid mixtures like water in butter. Solids dispersed in liquids give rise to suspensions of which several illustrations are to be cited. Solids may also be dispersed in other solids; colored precious stones and glasses are examples of this class.[2]

Dimensions of Colloidal Particles. Ultramicroscope.—Obviously the colloidal condition represents a transition state. In true solutions the attractive forces of solvent molecules upon other solvent molecules, and upon the molecules of the solute, are so balanced that solvent and solute, in a sense, lose their physical

[1] It is quite common to speak of certain substances, such as proteins, gelatine or glue, as colloids. This is an incorrect use of the term just as it is incorrect to call bromine a liquid. Bromine is liquid under certain conditions, solid or gaseous under others. The term liquid denotes a condition which is determined by external conditions and not by the chemical character of the substance alone. In the same way the term colloid denotes a condition which is determined by various factors to be described below. But just as substances, which under the usual conditions are liquid, may conveniently, although inaccurately, be called liquids, so substances which are most commonly encountered in the colloidal condition may be called colloids. Theoretically at least, all substances may be prepared in the colloidal condition, and presumably substances which usually exist in the colloidal condition may be obtained as solids, liquids or gases.

[2] Although glasses are strictly speaking super-cooled liquids, colored glasses are usually classified as suspensions of one solid in another.

identity; in a colloidal mixture, it is possible by the use of delicate methods to identify as separate units the particles of suspended material; in a coarse suspension casual observation is sufficient to show that the material is not uniform. Many colloidal mixtures seem as clear as true solutions to the naked eye; some are milky or opalescent. In some colloidal mixtures the suspended particles may still be seen with the aid of a microscope of high magnifying power; in others even the microscope fails to reveal the presence of suspended material. Under these conditions the **ultramicroscope** may be used to demonstrate the lack of homogeneity of the mixture.

The ultramicroscope makes use of a phenomenon which is very commonly observed. When a beam of light passes through a small opening into an otherwise darkened room, particles of dust seem to be suspended in the air, although under ordinary illumination the latter may appear quite clear. The dust particles scatter the light which falls upon them, and thus cause some of it to reach the eye. In this way the particles, although not really seen, give evidence of their presence. Similarly, the effect of a liquid on a transverse beam of light, observed against a dark background, is used to demonstrate the presence of suspended particles in a mixture. When a microscope is used as an aid in detecting the flashes of light caused by the particles, the combination of devices is called an ultramicroscope.

The smallest particle visible in a microscope has a diameter of about 0.00025 mm.; the smallest particle noticeable through the ultramicroscope is about 0.000006 mm. The latter figure is still many times the size of an average molecule, but indirect evidence has shown the existence in certain colloidal mixtures of particles too small to be observed even with an ultramicroscope. The limits of particle size in mixtures which are to be considered as colloidal are therefore quite indefinite; for convenience it is said that the particles range from those of the largest molecules to those which are just visible in the best microscopes.

Influences which Determine the Colloidal Condition.—The process of grinding, mentioned in connection with the conversion of a lump of clay into grains of colloidal size, is at best extremely tedious and in most cases unsuccessful. Most solids either resist extensive mechanical reduction of particle size or else the small

particles, momentarily produced by grinding, clump together with great readiness. When insoluble substances are formed by chemical reactions in solutions, they do not usually appear in grains small enough to prevent settling, and the small grains, even if originally produced, quickly form larger aggregates. Evidently colloidal mixtures can be formed and maintained only when the tendency to growth of the particles is in some way counteracted. Of course some substances may have a very small tendency to form large grains; in such cases colloidal suspensions may be formed simply by bringing together and agitating the components of the mixture.[1]

At least two simple mechanisms are known for stabilizing colloidal suspensions, that is, for preventing the small grains from clumping together or growing into larger ones. The suspended material is in many cases electrically charged. All of the particles carry the same kind of charge, and therefore repel each other instead of uniting to form larger grains. In other types of colloidal mixtures the suspended material behaves as if it were surrounded by a film which prevents particle growth. Further details of these mechanisms are described in the following paragraphs.

Adsorption.—The attractive forces between molecules diminish rapidly in intensity as the distance between the molecules increases. The forces in question nevertheless exert noticeable effects under certain conditions even on molecules of substances in the gaseous state (Chapter III). Certainly their influence must be much greater when the substances are in the solid or liquid state and two surfaces are exposed to each other, because then there are vastly greater numbers of molecules brought close to each other than when the substances are gaseous. When solid material is divided into the smallest possible particles, it has the largest surface per unit weight. It is therefore not surprising that solids when in the form of very fine, porous particles, hold gaseous or liquid substances at their surfaces. The phenomenon is called **adsorption.**

[1] Possibly even when colloidal dispersion appears spontaneously, impurities may be present in quantities minute but sufficient to overcome the tendency to agglutination.

Familiar instances of adsorption are found in many practical applications. Powdered charcoal, made extremely porous by special methods of manufacture, was used in gas masks during the war, not because it reacts chemically with poison gases, but because it adsorbs large volumes of them. Nitrogen and oxygen molecules on the other hand, are not readily attracted,[1] and consequently are not held back so readily by the charcoal. Another illustration is the use of the same substance as a deodorant for ice boxes, and the like. The vapors which cause the odors are probably moderately high boiling substances which are readily adsorbed. Adsorption by suspended solids may take place also from solutions. Bone black is used to decolorize sugar solutions; fuller's earth is used in a similar way. Sand filters appear to adsorb the bacteria and much of the insoluble impurities of water. The particles of charcoal, fuller's earth, or fine sand are very small, but they are large compared to the particles of colloidal suspensions. Obviously, adsorption must play an important rôle in the behavior of dispersed systems of all types.

Electrical Charge on Colloid Particles.—Since charcoal is used to separate poison gases from air, and coloring matter from sugar solutions, adsorption must be a selective process. This selectivity is shown by substances in the colloidal state, for some of them adsorb positive ions more readily than negative ions, and *vice versa*. A suspended particle which selectively adsorbs positive ions becomes positively charged, while one which adsorbs negative ions becomes negatively charged. The presence of ions is thus an important factor in the stabilization of certain types of colloids. Hydrogen and hydroxide ions are most often concerned. Mixtures of clay and a relatively small amount of water are made plastic by very low concentrations of sodium hydroxide, which keeps the solid clay particles in suspension. This is the method of preparing porcelain which does not shrink or become distorted greatly on baking.

Owing to the charges which they carry, particles of certain colloids migrate with the current. Positive colloids travel to the

[1] In general, substances of high boiling point are more readily adsorbed than those of low boiling point. There are cases however which do not follow this rule.

cathode, and negative ones to the anode. The phenomenon is called **cataphoresis.** The colloidal particles in general travel more slowly than do simple ions under the influence of the same potential difference, but the velocities are of the same order of magnitude. By noting the effect of the current, positive and negative colloids may be distinguished. Most of the insoluble hydroxides and sulfides of the metals form positive suspensions, while the noble metals, graphite, silicic acid and arsenous sulfide are negative. In some cases the charge on the particles varies under different conditions; it may be positive in slightly acid solutions as a result of the adsorption of hydrogen ions, while in alkaline solutions it may be negative as a result of adsorption of hydroxide ions. Besides being useful in determining the charge on the colloids, the effect of the current has been applied in industry, for example, in driving tanning fluids into hides and in settling clay suspensions from the water.[1]

Coagulation of Charged Colloidal Suspensions by Electrolytes. —Although colloidal particles may in general have a greater tendency to adsorb either negative or positive ions, the degree of adsorption is not dependent only upon the charge on the ions. It depends also on the chemical character and the concentration of the ions. Thus a negatively charged colloid like arsenous sulfide may adsorb positive ions from sufficiently concentrated solutions of electrolytes. The positive charge thus acquired neutralizes the negative charge originally present. Under these conditions the repulsion between like charges, which prevented the smaller particles from growing into larger ones, is eliminated. As a result, the colloidal suspension **coagulates,** and the larger particles settle out as a flocculent or amorphous precipitate. Hydrogen ions are particularly readily adsorbed, and their effect may easily be observed by the addition of a small amount of hydrochloric acid to a colloidal suspension of arsenous sulfide. Sodium hydroxide on the other hand coagulates positive colloidal ferric hydroxide.

[1] In tanning, electro-endosmosis is more important than cataphoresis. When two portions of a colloidal mixture are separated by a membrane which allows the passage of the pure liquid, but not of the suspended, electrically charged colloidal particles, the liquid is transported by the current. The phenomenon is called electro-endosmosis.

The interpretation just given for the coagulation of charged colloids by electrolytes is borne out by the coagulating effect of ions of different valence. Negative colloids are more readily coagulated by salts containing a bivalent positive ion than by those containing a univalent positive ion, and salts containing a trivalent positive ion are still more effective. The valence of the positive ion is without influence in the coagulation of positive colloids; in this case, however, the valence of the negative ion is the determining factor.

The usefulness of aluminium sulfate (alum) in water clarification is due in part to the fact that it yields both polyvalent negative and positive ions, and is therefore effective in coagulating both positively and negatively charged suspensions. Where rivers debouch into the sea the deposition of silt, which used to be ascribed entirely to the slowing down of the current, is now seen to be due in part to the coagulating effect of the salts in sea water. On the other hand, the removal of salts often causes a coagulated colloid to return to the highly dispersed condition. When sulfides are precipitated from salt solutions, the presence of the other ions prevents the formation of unfilterable suspensions. As the precipitate is washed, the salts are removed, and the precipitate often begins to run through the filter as washing approaches completion. To avoid this difficulty, washing is often carried out with ammonium nitrate solution instead of pure water.[1]

Clearly the same effect produced by ions could also be brought about by charged colloids. When a suspension of positively charged material is mixed with a negatively charged one both are coagulated. Many dyes are colloidally dispersed rather than dissolved in water, and are adsorbed by the fibers of the textiles on which they are used. Often such dyes are not "fast"; that is, they are removed from the fiber by water. In such cases a mordant like aluminium sulfate is used. The aluminium sulfate diffuses into the fibers. Since it is partially hydrolyzed, it furnishes aluminium hydroxide which, as a positive colloid, coagulates dyes consisting of negative colloids.

[1] Ammonium nitrate is used because it may readily be removed later by heating the precipitate; hence it is unobjectionable in the course of analysis.

Emulsions.—Although it is fairly easy to mix two mutually insoluble liquids by vigorous stirring, a mixture consisting of two such liquids alone is not stable.[1] Surface tension always operates to make the surface of a liquid as small as possible; consequently small drops coalesce to form larger ones, since a single large sphere has a smaller surface than a large number of smaller ones of the same total volume. It is, therefore, always necessary to stabilize the mixture by adding an emulsifying agent, which is usually a substance in the colloidal state.

A number of hypotheses have been advanced to explain the action of the emulsifying agents; of these only the following one is taken up. Substances which lower the surface tension at the surfaces between two liquids not only decrease the tendency toward formation of larger drops, but also stabilize the film which exists between the suspended droplets and the dispersing medium. Substances which lower the surface tension are strongly adsorbed into the surface of the solution; that is, the surface layers of solutions of such substances become more concentrated than the interior of the liquid. Thus the surface tension of soap solutions is less than that of pure water, and decreases with the age of the solution, showing that the soap is gradually drawn into the surface. Consequently a fresh surface, made by partially rupturing an old one, has a higher surface tension than the old one had. As a result, whenever anything happens to break the soap film it becomes automatically stronger. Soap therefore acts as an excellent emulsifying agent, as shown by the lather formed when air and a soap solution are mixed. The albumen in egg or the casein of milk have similar effects which are important in baking.

Two given liquids may form two types of emulsion. Thus oil drops may be dispersed in water or water droplets dispersed in oil. Two factors are of importance. In the first place the liquid present in the smaller amount tends to be the dispersed phase, that is, to form the droplets. In the second place the nature of the emulsifying agent plays an important rôle. The following considerations should make this clear.

An emulsifying agent like soap is made of very large molecules. In soap molecules there is a long chain of carbon and hydrogen atoms with a carboxyl group, COOH, at one end.[2] The chain of carbon atoms is

[1] Very dilute emulsions are sometimes stable even in the absence of an emulsifying agent.

[2] In the soap itself, the hydrogen ion of the COOH group is of course replaced by a positive ion of a metal.

like a hydrocarbon molecule, and is often called a hydrocarbon chain. Hydrocarbons are probably the most nearly completely non-polar compounds known. On the other hand the carboxyl group is polar as shown by the fact that the hydrogen is ionized, and that the soaps are true salts of the long chain organic acids. According to the generalization discussed on pages 126–129, polar substances should dissolve in polar ones, and non-polar substances should be soluble in other non-polar ones. At a surface between an oil, that is a hydrocarbon, and water, a soap molecule ought to orientate itself in such a way that the polar COOH group, or the corresponding salt group, COOMe, would lie in the water surface, and the hydrocarbon chain in the oil, as shown in Fig. 23. Suppose now that the hydrocarbon chains of the soap molecules are

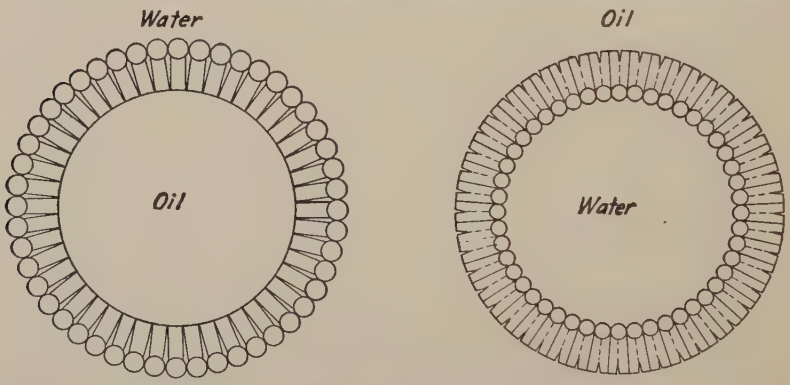


FIG. 23.—ILLUSTRATING THE HYPOTHESIS DESCRIBED FOR THE INVERSION OF EMULSIONS

The circles represent the polar groups of the emulsifying agent, and always point to the water surface in an oil and water mixture.

wider than the polar group. As shown in Fig. 23, such a condition forces the water surface to be convex, and causes the water to form droplets in the oil. If, on the other hand, the polar group is wider than the chain, the water surface must be concave to accommodate the larger polar group, and the oil is forced to form the droplets.[1]

[1] The statement that these interpretations are still in the realm of hypotheses rather than of established fact is again called to the students' attention. More detailed development of these ideas is found in the following: Langmuir, Met. Chem. Eng. **15,** 468 (1916), Journal of the American Chemical Society **39,** 1848; Harkins, Davies and Clark, *ibid.*, **39,** 354, 541; Finkle, Draper and Hildebrand, *ibid.*, **45,** 2780; and Harkins and Keith, Science **49,** 463–7 (1924).

Jellies and Gels.—The amounts of liquid which may be dispersed in other liquids in the presence of emulsifying agents are much greater, in many instances, than the amount of solid material which can usually be dispersed in a liquid. Emulsions of kerosene in water have been prepared which contain 98 per cent of kerosene and only 2 per cent of water, and yet the latter must be looked upon as the dispersing medium for the oil drops are surrounded by water. In such emulsions the drops are so close together that they become deformed, and the two liquids no longer slip over one another freely. This results in the formation of a somewhat elastic, jelly-like material. Jelly formation is, however, in many cases a much more complex phenomenon, the nature of which is still in dispute. Evaporation of a suspension of soap in water ultimately leads to the formation of a semi-opaque jelly. This seems to consist of cell-like structures or of long streamers of material dispersed through the main body of the mixture. The "cell walls" or streamers may consist of partially dehydrated substances. Gels are irregular lumps of a nature similar to that of jellies.

Protective Colloids.—When a solid is suspended in a liquid which contains a colloid of the emulsion type, the drops of suspended liquid enclose the suspended solid, and the latter behaves like an emulsion colloid. For this reason the addition of emulsion colloids to liquids aids in the stabilization of suspension colloids. The emulsion type is used under these condistions as a **protective colloid.** Silver particles may be kept in suspension by gelatine; the mixture is sold as protargol. Soap aids in the suspension of solid particles because the emulsion it makes with the oil or grease on hands or clothes encloses solid dust particles.

Preparation of Substances in the Colloidal Condition.—Methods for preparing substances in the colloidal state may be divided into two broad classes, the **dispersion** and the **condensation** methods. In the former, larger particles are disintegrated into smaller ones. In carrying out a method of this type it is necessary to take into account the tendency of the smaller particles to combine to larger aggregates. Conditions which prevent particle growth must be maintained. Colloidal suspensions of the less active metals may be prepared by passing an arc between

electrodes of the metal under water. The metal is volatilized in the arc, and the vapor very rapidly condensed by contact with water. By this rapid condensation very minute particles of metal are formed. Enough ions are present in the water to allow the colloidal particles to assume a charge which prevents aggregation to larger particles. In some cases the addition of a protective colloid is desirable.

Actual grinding is another illustration of the dispersion method. In order to make the grinding more effective, the substance to be dispersed is mixed with another substance soluble in the dispersing medium. The added substance makes it possible to grind smaller. It is removed, because of its solubility, when the mixture is added to the dispersing medium. Colloidal suspensions of sulfur have been made by grinding sulfur with urea, and then adding water to the mixture. The sulfur remains in suspension, the urea dissolves. It is of course essential that the substance added to facilitate grinding be one which does not coagulate the suspension; in general non-electrolytes must be used.

Many substances may be colloidally dispersed by the aid of a **peptonizer,** a substance which causes the formation of colloids. The use of small amounts of sodium hydroxide in dispersing clay (already briefly described) is an illustration of this type of method. In some instances the dispersing medium itself or the substance to be dispersed may act as peptonizer. Gelatine, glue, and so on, become colloidally dispersed when simply mixed with water. These substances are probably slightly soluble in water, and tend to reduce the surface tension at the interface between the undissolved suspended portion and the liquid. They thus stabilize the interfacial film.

Condensation methods start with substances in the molecular condition, for example in solution, and build up colloidal particles. Here it is necessary to prevent the continued growth of particles to too large a size. A number of methods are possible. When the colloidal mixture is of the suspension type, particle growth is in general prevented by charges upon the grains. High concentrations of electrolytes counteract this charge, and coagulate the suspension. For this reason reactions in which one of the reaction products is to be obtained in the colloidal state should be

so planned that no strong electrolyte is present at any time. The reaction between arsenous acid and hydrogen sulfide is of this type:

$$2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O$$

Both arsenous acid and hydrogen sulfide are but slightly ionized; of the reaction products, water is likewise a very weak electrolyte, and arsenous sulfide is insoluble. As a result the sulfide obtained is colloidal. Reduction of metal salts by organic reagents leads in many instances to the same result. When it is impossible or inconvenient to choose a reaction in which low ionic concentrations are used throughout, a protective colloid may be added or the reaction so chosen that a protective colloid is formed. The addition of a little gelatine to silver nitrate before the addition of a chloride causes the silver chloride to remain colloidally suspended.

A very interesting method is one involving **dialysis.** Membranes are known which permit certain substances, but not others, to pass through them. Parchment for example permits water and some electrolytes to pass freely, but does not allow the larger colloidal particles to penetrate. When ferric chloride is dissolved in water limited hydrolysis takes place, as shown in the equation:

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

If the solution is placed into a tube made of parchment, and the whole is dipped into pure water, the hydrochloric acid diffuses out into the surrounding water. Consequently, hydrolysis continues, and at the same time the electrolytes are removed. Finally a colloidal suspension of ferric hydroxide is left in the parchment tube.

Colloid Chemistry.—As has been emphasized in the preceding pages, the essential characteristics of substances in the colloidal condition depend upon extremely small particle size and relatively large surface areas in intimate contact with each other. For this reason, phenomena which are often overlooked with less finely divided materials, may assume predominating importance in the case of colloids. The study of these phenomena and of the behavior of substances in this condition is called colloid chemistry. Attractive forces between molecules, factors which influence vis-

cosity of solutions, surface tension, etc., must be included in the subject. It is evident therefore that colloid chemistry lies on the borderline between physics and chemistry, and that cooperation between the two sciences is essential to the solution of the many problems to be solved. These problems are of the greatest interest from both theoretical and practical points of view. In their minute size, colloidal particles approach the condition of the molecules themselves, and further study of colloidal suspensions is bound to lead to a more complete understanding of the forces which control molecular behavior. The attractive forces which determine adsorption and many of the phenomena of colloid chemistry are closely related to chemical forces; hence the development of colloid chemistry will lead to the advancement of chemistry as a whole.

Colloid chemistry plays a vastly important rôle in nature and in industry. The proteins are present in the body as colloids and many of their reactions are largely matters of coagulation and peptization. Gelatinous silicic acid unquestionably has played a rôle in geologic processes; many lavas are colloidal mixtures, and the formation of fogs and mists is another instance of the importance of colloid chemistry to geology. Industrial applications are met at every hand. Glues and gelatine, photographic emulsions for plates and films, many inks, dyes, paints, varnishes, cement, celluloid, paper, and thousands of other materials in common use are colloidal. The matter of lubrication is a problem of adsorption of films on metal surfaces. The flotation process for separating ores from tailings by wetting the ores with oil and the tailings with water (thus causing the former to float and the latter to sink) is another important application of colloid chemistry. Manufacture of porcelain and tanning have already been mentioned. It is manifest from this brief survey that a short chapter can serve only to indicate the problems and applications of colloidal chemistry, and that the subject is one which should be further studied in texts devoted to it. A list of these is given below.

Osmosis and Osmotic Pressure.—In connection with the preparation of substances in the colloidal condition, dialysis by means of **semi-permeable membranes** was mentioned. These are

membranes which allow some substances but not others to pass through them. Suppose that a sack, made of such a membrane, is dipped into pure water, while the interior of the sack contains a colloidal suspension. The molecules of pure water diffuse uninterruptedly in all directions and must, in the course of their movements, strike the surface of the sack and penetrate into it. The water molecules within the sack, however, encounter particles of the suspended material which interfere with their free diffusion toward the walls of the sack. Consequently, the water should flow more freely into the sack than out of it, and an actual movement of the water into the suspension should be observable, if conditions are properly chosen for the experiment. The flow of a liquid through a semi-permeable membrane into a mixture containing that liquid is called **osmosis.** Suppose that the sack is firmly attached to a vertical tube. As the water flows into the sack the liquid must rise in the tube. The hydrostatic pressure thus developed will ultimately be great enough to counteract the tendency of the pure liquid to flow into the sack. This pressure is known as the **osmotic pressure** of the **mixture.**

The osmotic pressure of colloidal mixtures is very small—too small in fact to be observed except with very delicate apparatus. The reason for this is easily understood. Although the colloidal particles in a suspension or an emulsion seem very numerous compared to ordinary objects, their number is small when compared to the number of molecules of the solvent, or dispersing medium, which in the illustration cited was water. For this reason the number of impacts of water molecules outside the membrane is not so very different from that on the inside, and the osmotic pressure is therefore very small. In the case of true solutions the case may be made quite different, if very soluble substances are used, for in that case the number of dissolved molecules may be made large even in comparison to the number of those of the solvent. Now there are membranes which allow pure water to penetrate but are relatively impermeable to certain solutes. Thus parchment is permeable to water and not to sugar. When a sugar solution is used in the device described above, the liquid rises to considerable heights in the tube, showing that the solution has a very considerable osmotic pressure.

Since, under the simplest conditions, osmotic pressure is determined by the number of impacts between solvent and solute molecules, the osmotic pressure must be proportional to the number of solute molecules. In some very dilute solutions, the osmotic pressure obeys a law quite similar to the gas laws, namely $Pv = NRT$, in which P is the osmotic pressure, N the number of gram molecules, and R a constant which has the same value as for gases. In other words, a substance in solution exerts the same osmotic pressure as it does in the gaseous state at the same concentration and temperature. But this statement applies only to the simplest conditions which are rarely encountered. Owing to attractive forces between solvent and solute molecules, to adsorption at the membrane surface, and to a variety of other causes there is usually a very considerable deviation between the equation and the actual facts. The situation is too complex for further discussion.

There are a number of interesting applications of osmosis and of osmotic pressure. In chemistry, the chief application has been to the determination of molecular weights of dissolved substances. But this application has been very limited, both because of the deviations from theory, and because of the difficulty in making accurate measurements.[1] Electrolytes like sodium chloride in very dilute aqueous solution exert approximately twice the osmotic pressure required by the equation and their formulae; this is, of course, only another evidence that such substances are dissociated in solution. In biology, osmosis and osmotic pressure have been the subject of an immense amount of discussion and experiment. The passage of salts and of food molecules from the blood stream to the cell, the flow of sap through plants, and other similar fundamental phenomena are unquestionably related in part to the osmotic pressure differences between cells and fluid stream. A cell placed in a salt solution of the same osmotic pressure as that which normally bathes it undergoes no change; one placed in a solution of higher osmotic pressure will dry out by giving up its water through the semi-permeable cell wall to the

[1] Considerations based on osmotic pressure have been used to develop a theory of solutions. This phase of the subject is treated in text books of physical chemistry.

more concentrated outer solution; one placed in pure water may burst because the water diffuses into the cell and causes swelling. These phenomena again are extremely complex; the cell walls are semi-permeable to some substances, not to others; the semi-permeability is not perfect and is determined by a variety of biological conditions. Nevertheless the field is one of the greatest importance to biology and medicine.

EXERCISES

(1) In what respects do colloidal suspensions differ from true solutions and in what respects from coarse suspensions?

(2) What prevents the settling of colloid particles?

(3) Explain the origin of the charges on colloid particles and show how the charges prevent coagulation.

(4) Calculate the surface of material contained in a cube with edges 1 centimeter long. Suppose this cube were divided into cubes with edges 0.1 centimeter long; how many cubes would there be and what would be the total surface?

(5) Explain why, in general, substances of high boiling point are more readily adsorbed than those of low boiling point.

(6) Explain the action of electrolytes in coagulating colloids.

(7) Name some salts which should be effective in coagulating positive colloids.

(8) Suggest a reaction by means of which zinc sulfide could be obtained in the colloidal condition.

(9) Explain the cleansing action of soaps. Take into consideration that the average spot on soiled materials consists of grease and solid dirt.

(10) What is a jelly?

(11) Name the two general methods for producing colloidal suspensions or emulsions. Illustrate each.

(12) Assuming that sugar in solution obeys a law identical with that of gases, calculate the osmotic pressure of a 0.1 per cent sugar solution. Assume the density of the solution to be equal to that of pure water. The molecular weight of sugar is 342. The temperature is 15°.

REFERENCES

Since colloid chemistry is a complex subject, involving not only physical chemistry, but physics as well, most books devoted to it are not suitable for collateral reading by students of general chemistry. The first two

of the following references are short chapters in general chemistry texts by authors who have worked in the field of colloids. The third is a very readable book on colloids, most of which is devoted to descriptions of applications of colloid chemistry to other sciences, and to industry and daily life. The fourth is more theoretical; it is in fact the theoretical part of a projected series of books on the subject, but it is largely non-mathematical in treatment. The last reference is to a book written by a number of collaborators under the editorship of Bogue. As is always true in such cases, the treatment by the various authors is not the same, and some portions are less technical than others. It is added to the list for completeness, rather than to be used by the readers of this text at present.

Holmes—General Chemistry (1921) Chapter XXV.
Hildebrand—Principles of Chemistry (1918).
Alexander—Colloid Chemistry (1924).
Bancroft—Applied Colloid Chemistry, Theory (1921).
Bogue—Colloidal Behavior (1924).
See also Rogers, Industrial Chemistry, Chapter L.

CHAPTER XXX

SILICON AND BORON

The elements silicon and boron are in many respects similar to carbon. Silicon exists in a crystalline modification in appearance very much like graphite. It has also been prepared in an amorphous form, which is like those varieties of carbon formerly thought also to be amorphous. A modification of silicon said to be of the same crystalline structure as diamond has been described, but the correctness of the observations is somewhat doubtful. Boron, too, exists in amorphous and crystalline modifications, and the latter likewise resembles graphite in its black luster. Both silicon and boron, especially in the amorphous condition, are very much more reactive than is carbon. Neither of the two is ever found free in nature. They are prepared from the oxides or halides by treatment with active metals such as aluminium, magnesium or the alkali metals. Silicon is now manufactured by heating silicon dioxide (sand) with coke in an electric furnace. It is used in making alloys. Duriron contains 14 per cent of silicon. The silicon seems to make the iron extraordinarily resistant to the action of acids, and the alloy is used in condensers employed in the manufacture of nitric acid. Ferrosilicon, another alloy of iron and silicon, is used to remove air bubbles from steel during its manufacture. Boron is difficult to prepare pure, and no uses for the element are known.

The similarity of elementary silicon and boron to carbon extends in a measure to their compounds, but the resemblances in the compounds are more formal than real. However, both the resemblances and differences are in many instances the very ones to be anticipated from the periodic system. Silicon is in the same group as carbon and therefore resembles it in certain respects;

the likeness of boron and silicon is another illustration of the fact that the first member of an outer group is often more like some element of the subsequent group than like others of its own family.

Silicon Dioxide and the Silicic Acids.—Crystallized silicon dioxide is widely distributed in nature as quartz. Sometimes huge crystals are found; others are colored by impurities as in smoky quartz or in amethyst. When quartz is heated, it is transformed into other crystalline modifications of silicon dioxide which need not be mentioned here in detail. The transformations are extremely slow, and if the heating is carried out rapidly, the quartz begins to soften long before its melting point is reached. In this condition it may be molded into vessels of various shapes. Opaque quartz apparatus is manufactured in this way. At about 1780°, the rapidly heated quartz becomes quite fluid. This liquid can be greatly supercooled, and forms a transparent glass-like material, known as transparent quartz, of which laboratory apparatus is also made. Quartz apparatus has three advantages over that made of ordinary glass. It contains no alkali, and may therefore be used in experiments in which even the small traces of alkali dissolved from glass are objectionable. In the second place, it has a much higher melting point than glass. Finally, since it has a very small coefficient of expansion, it contracts very little on cooling. For this reason hot quartz vessels may be suddenly chilled without cracking; a red hot quartz beaker or flask may be plunged into cold water without damaging the apparatus.

Silicon dioxide exists also in natural amorphous modifications. These are often colored by oxides of iron as in agate or onyx. Opal and flint are slightly hydrated varieties. Certain organisms produce a form of the dioxide known as diatomaceous earth (Kieselguhr) which is used as a scouring powder and as a decolorizer of oils.

Silicon dioxide is chemically quite inert. It reacts slowly with solutions of alkalies; more rapidly with fused alkalies. It displaces carbon dioxide from molten carbonates. It does not react with acids except hydrofluoric acid (see page 165). The differences between silicon dioxide and carbon dioxide are striking. The former is a solid up to very high temperatures, the latter a gas

under ordinary conditions; the former is inert and insoluble in all solvents while the latter is moderately soluble in water and other liquids, and is chemically quite active. The differences are due to the fact that silicon compounds have a great tendency to **polymerize,** that is to form aggregates of large molecular weight. Thus the molecular weight of silicon dioxide is unquestionably much greater than corresponds to the simple formula SiO_2. The formula should really be $(SiO_2)_x$. Carbon compounds also polymerize in many instances, but the tendency to do so is much more limited.

Silicic Acid.—Silicon dioxide does not react with water, although certain amorphous preparations are capable of adsorbing large quantities of the latter. Nevertheless it is considered the anhydride of silicic acid, for when it is boiled with alkalies, it yields salts like sodium metasilicate, Na_2SiO_3. The unstable silicic acid from which these and other salts are derived is a very weak acid. The aqueous solutions of the salts are extensively hydrolyzed, and are therefore strongly alkaline; even the very weak carbonic acid displaces silicic acid from them. Silicic acid thus liberated appears in the form of a colloidal suspension. Under certain conditions the colloidal particles enclose so much water and the films are so rigid that stiff gels are produced. When these are heated, water is gradually lost until completely dehydrated silicon dioxide remains. It was once thought that during the process of dehydration various silicic acids, such as orthosilicic acid, H_4SiO_4, disilicic acids, $H_4Si_2O_6$ and $H_2Si_2O_5$, trisilicic acid, $H_4Si_3O_8$, and metasilicic acid, H_2SiO_3, were formed. But the loss of water is perfectly gradual, and there is no real evidence for the existence of these various acids.

Silicates.—One of the facts which led to the belief in the existence of the various silicic acids is that many of the natural silicates have formulae which correspond to salts of those acids. Thus kaolin may be formulated as an acid orthosilicate of aluminium, $H_2Al_2(SiO_4)_2 \cdot H_2O$, and mica as an acid potassium aluminium orthosilicate, $KH_2Al_3(SiO_4)_3$; asbestos as a calcium magnesium metasilicate, $CaMg_3(SiO_3)_4$; serpentine as a magnesium disilicate, $Mg_3Si_2O_7 \cdot 2H_2O$, and so on. This classification is, however, purely formal. It is probable that the silicates belong to a class

of complex compounds, the constitution of which is at present not thoroughly understood (see page 574).

Silicates are, however, of great importance both in nature and in industry. The minerals mentioned are but a few of a vast number which make up a large part of the earth's crust. Bricks and tiling are made of common clay, which is an impure form of kaolin; porcelain and china are made of the purer forms. The tendency of clay to form colloidal suspensions in water and the plasticity of the resulting mixtures have already been mentioned in the discussion of colloids. Cement and concrete consist of particles of silica and silicates held together by calcium and aluminium compounds. **Glass** is a mixture of silicates, usually of sodium and calcium, in the form of supercooled liquids. Glasses of different properties to suit various purposes are made by adding various substances to ordinary glass. By substituting lead and potassium for sodium and calcium, flint glass, used in optical work, is prepared. It is used also for making " cut glass." Particularly strong, high melting or insoluble glasses, such as pyrex or Jena, contain some boron trioxide in place of part of the silica. Glass is colored by adding colored compounds; cobalt oxide for blue glass, gold, selenium or cuprous oxide for red, and so on. Enamels are glasses made white by suspending in the silicate melt substances like tin oxide or calcium phosphate, which are insoluble in this medium.

The Halides of Silicon.—Silicon forms with all of the halogens, tetrahalides, analogous in formula to the tetrachloride, $SiCl_4$. The tetrachloride and tetrabromide may be prepared by the action of chlorine and bromine on silicon; the tetrafluoride may be prepared in the same way or by the action of silicon dioxide on hydrofluoric acid (page 165). The chloride, bromide, and iodide are volatile liquids at ordinary temperatures, while the fluoride is a gas. All of them are hydrolyzed by water to the corresponding halogen acids and hydrated silicon dioxide. It will be recalled that carbon tetrachloride does not act with water readily. The difference may be accounted for by the assumption that the halides of silicon, although exceedingly slightly ionized, nevertheless possess salt-like character. On this assumption they are the salts of the exceedingly weak base, silicic acid; the corresponding

carbon compounds are not salt-like, and carbonic acid must be looked upon as entirely lacking in basic character. Since silicon has a higher atomic weight than carbon and both are members of the same outer group silicon should be more electropositive than carbon. Its hydroxide should therefore be somewhat more basic than that of carbon, and its compounds with electronegative elements more salt-like than those of carbon.

In the reaction between silicon tetrafluoride and water a secondary reaction takes place in which **fluosilicic acid** is formed.

$$SiF_4 + 2H_2O \rightarrow Si(OH)_4 + 4HF$$

$$2HF + SiF_4 \rightarrow H_2SiF_6$$

Fluosilicic acid exists only in solution, but some of its salts are quite stable. Potassium fluosilicate is one of the few potassium compounds insoluble in water. It is sometimes used in analytical work.

The Hydrides of Silicon.—Silicon forms a fairly large number of hydrogen compounds called **silanes** or silicon hydrides. Owing to experimental difficulties encountered in working with them, these compounds have not yet been fully investigated. Their formulae correspond to those of the paraffine hydrocarbons; thus monosilane is SiH_4, disilane Si_2H_6, trisilane Si_3H_8, and so on. Only seven or eight compounds of this group have been definitely identified, and none is known with certainty to correspond to the unsaturated hydrocarbons.

In these compounds, silicon shows a tendency like that of carbon to form chains. But in most respects the silicon hydrides are not very similar to the hydrocarbons. The tendency for silicon atoms to link with other silicon atoms is not very pronounced, as shown by the fact that disilane breaks down into monosilane and hydrogen at moderate temperatures, and that trisilane decomposes under ordinary conditions to the lower hydrides. In contrast with the great inertness of hydrocarbons, the silicon hydrides are extremely reactive. Most of them are spontaneously inflammable in air; they react violently with the halogens; they are decomposed by water containing traces of alkali into hydrated

silicon dioxide and hydrogen; and they react with hydrogen chloride to give halogen derivatives and hydrogen, e.g.:

$$Si_2H_6 + HCl \rightarrow Si_2H_5Cl + H_2$$ [1]

These differences are explained in part by the fact that silicon, as the second member of the fourth outer group, is more electropositive than is carbon. It has not the marked tendency of carbon to be equally electropositive and electronegative, and consequently the compounds formed by sharing of electrons between two silicon atoms are not so stable as the corresponding carbon compounds. For this reason long chain or ring compounds of silicon are not numerous. On the other hand, silicon compounds such as the hydrides display a marked tendency to go over into others in which the silicon is the electropositive constituent, as in the halides and oxide.

Silicon and Carbon Compounds in Nature.—The peculiar characteristics of carbon permit it to form a vast number of compounds of varied nature, adapted to the many functions of living organisms; in many instances the sluggishness with which these substances react enables them to exist in contact with air and with water, and to resist the action of body fluids; on the other hand, many of the carbon compounds react readily in the presence of catalysts, and therefore take their part in metabolism. The end product of the reactions in the body is carbon dioxide. Since this is volatile, soluble and reactive, it again enters into life processes. Silicon compounds, for the reasons given above, are not so numerour nor so varied; most of them are decomposed by air and water; the final product of their reactions is silicon dioxide, which is non-volatile, insoluble and non-reactive. It is obvious that life based on silicon compounds would have to be very primitive and simple. On the other hand, the insolubility of silicon dioxide and the silicates permits them to resist the erosive action of rain and seas, and consequently makes them important constituents of the inorganic world.

Boron Compounds.—The compounds of boron are in most respects quite similar to those of silicon except for differences in

[1] This reaction occurs only in the presence of catalytic agents such as aluminium chloride.

solubility, and formula. The latter difference is due to the fact that boron is usually trivalent and silicon tetravalent. The oxide, B_2O_3, unlike silicon dioxide is soluble in water and unites with it to form **boric acid**, H_3BO_3, a slightly soluble, very weak acid. It is used in medicine as a mild antiseptic. The formulae of the borates, like those of silicates, seem to point to the existence of a number of complex acids, but the structure of these salts is also not well understood. The most common salt is borax, $Na_2B_4O_7 \cdot 10H_2O$, extensive deposits of which are found in the dry areas of the West. A large portion of the supply of boron compounds is manufactured from colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$, found in California.

As the salt of a weak acid borax is appreciably hydrolyzed, and gives a strongly alkaline reaction in aqueous solution. Most of the borates, except those of the alkali metals, are but slightly soluble in water. The addition of borax to water containing ions of the heavy metals, therefore removes these ions from solution. For this reason borax is used in laundry work to soften water (page 493). It is also used in soldering to remove oxides from the surfaces of metals. Borax is an acid salt as shown by writing its formula $2NaBO_2 \cdot B_2O_3$. When borax is melted with basic oxides. such as that of copper, the latter unite with the acid oxide, B_2O_3, to form salts. In this way the borax removes the surface layers of the oxide. In analytical chemistry, borax beads are extensively employed. Cobalt oxide, for example, reacts with borax just as does copper oxide, and the mixed salt, $2NaBO_2 \cdot Co(BO_2)_2$, thus obtained forms a blue, transparent, glassy material by means of which the cobalt may be identified. The use of borax in glass and enamel has already been mentioned.

The hydrides of boron, although little investigated, seem to be compounds of extraordinary theoretical interest. Their properties are very much like those of the silicon hydrides. The most important fact in this connection, however, is that in the hydrides, the valence of boron seems not to be the same as in the simple boron compounds. The formulae of the hydrides thus far studied are B_2H_6, B_4H_{10}, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$. The boron is clearly not trivalent, nor is it possible to say what valence is to be ascribed to the element in these substances. It is clear, however, that to some extent, boron shares with carbon and

silicon the tendency to form chain compounds. The **halides of boron** also resemble closely the corresponding silicon compounds, except in formula.

EXERCISES

(1) Point out in what respects carbon and silicon are alike, and in what respects they differ. To what extent are the differences observed in accordance with the regularities of the periodic system?

(2) What properties of carbon and of silicon compounds account for the different rôles which the two elements play in nature?

(3) Point out the similarities between silicon and boron.

(4) What is opaque quartz glass? Transparent quartz glass?

(5) What is the experimental evidence that silicic acid is a weaker acid than carbonic acid?

(6) Why is borax used as a flux in soldering?

(7) Suggest a method for preparing silicic acid from any of the silicon compounds found in nature. Answer the corresponding question for boric acid.

REFERENCES

Lowry—Inorganic Chemistry. Chapter XXIX, in addition to the compounds of silicon and boron of theoretical interest, describes also the occurrence of silicates and borates in nature and their uses in industry.

Rogers—Industrial Chemistry. Chapters X, XI, and XII deal with lime, cement and plaster, clay, brick and pottery, and glass respectively. These chapters, therefore, deal with compounds of silica and the alkalies, alkaline earths, aluminium, etc., and are collateral reading for later chapters of this text as well as for this one.

CHAPTER XXXI

THE METALLIC ELEMENTS

Alloys

From what has already been said about the metals it is evident that they are the more electropositive elements, or in other words, that they are composed of atoms which readily lose electrons. The arrangement of the periodic system brings this fact out clearly; thus, in the outer series, the metals are found in the earlier groups or among the elements of higher atomic weight in the other groups.

Some of the Physical Properties of the Metals.—Several of the most important physical properties of the metals are very direct consequences of the tendency of their atoms to lose electrons. Thus when the more active metals are exposed to ultra-violet light, electrons are actually given off from the metallic surface (**photo-electric effect**), and a similar phenomenon occurs when the metals are heated. The construction of the audion tubes used in radio-telephony is based upon this fact. Metals are **conductors of electricity,** and the passage of the electrical current through them is not accompanied by any noticeable chemical changes or by transport of weighable quantities of matter. The explanation of this phenomenon is that in a mass of metal there are enough loosely held electrons so that the application of a potential difference causes the electrons to drift towards the positive pole, thus carrying the current. A number of theories have been advanced to describe the mechanism of the passage of the electrons through the metal; it is, however, unnecessary here to go into a discussion of the details.

According to the electromagnetic theory of light, any metallic conductor must also reflect light in the way characteristic of metals. Thermal and electrical conductivity are likewise related

phenomena; both the metallic **luster** and high **thermal conductivity,** which quite sharply distinguish metals from the non-metals, are therefore also related to the fundamental characteristic of the atoms of metallic elements.

The metals possess a number of mechanical properties which differ quite decidedly from those of non-metals. The typical metals are tenacious, ductile, elastic and malleable, whereas most of the non-metals are brittle. In other physical properties such as hardness, volatility, melting point, etc., the metals do not display any common character; the melting points, for example, are related to the positions of the elements in the periodic system rather than to specific metallic properties. They are in general quite high. It is to be noted, however, that mercury is liquid at ordinary temperatures, gallium melts at about 30°, and the alkali metals have fairly low melting points. Most metals crystallize in the cubical system.

None of the typical metals shows any properties which indicate that they take on electrons or that they have a very pronounced tendency to unite with other elements by electron sharing. It is, on this account, easy to understand why the free metals should be monatomic, in contrast to the non-metals which in the free condition almost invariably exist as polyatomic molecules. Since the metals are highly polar they should dissolve only in other polar compounds; as a matter of fact, they are with but few exceptions soluble only in one another.[1]

The Characteristic Chemical Properties of the Metals.—Since the atoms of the metals readily lose electrons, they must **readily form positive ions in solution.** On the other hand, these atoms do not take up electrons to form ions, as shown by the fact that the metals never form simple negative ions. Some of the metals enter into compound negative ions such as permanganate and chromate ions. Views concerning the mode of union of the

[1] The alkali metals are soluble in liquid ammonia. They would probably also dissolve in water if the chemical action between them and this solvent could be prevented. One must distinguish sharply between dissolving in a solvent and reacting with it to give a soluble product. The statement that some metals are dissolved by acids is inaccurate; they react with acids. Likewise the fact that it is easy to prepare colloidal suspensions of metals in liquids must not be confused with true solubility.

atoms in such ions have been discussed in Chapter XXIV; in none of them is it ever assumed that the metal constitutes the negative component. In losing electrons the metals must **act as reducing agents**; they are never oxidizing agents, since they do not take on electrons. The **hydroxides of the metals,** in accord with the electropositive character of the elements, are essentially **basic** in character. For this reason their chlorides (which are salts of the strong hydrochloric acid) are not completely hydrolyzed, as are the chlorides of non-metals such as sulfur or phosphorus.

Degrees of Metallic Character.—The elements of an outer *series* of the periodic system decrease in positive character and increase in tendency to be electronegative by graded steps with ascending atomic weight; within an outer *group* increase in electropositive character accompanies increase in atomic weight of the elements. It is therefore not to be expected that the positive and negative elements should form two sharply distinct groups. The properties described as characteristic of the metallic elements are more marked in some than in others, depending on their position in the periodic system.

Gradual appearance of metallic properties has been described in the nitrogen group. The first two members, nitrogen and phosphorus, are non-metallic, they do not exist as free positive ions in solution, and their hydroxides are acids. Arsenic and antimony exist in both metallic and non-metallic modifications; positive arsenous ion is shown to exist by the precipitation of arsenous sulfide from solution, and antimony forms salts (like the chloride and nitrate) in which antimony is the positive ion; arsenous acid displays very slight basic properties while antimonous hydroxide is more basic than acid in character. Bismuth exists only as a metal; it forms only positive ions; its hydroxide is exclusively basic. Thus bismuth is the most metallic of the group as judged by any of the criteria mentioned. But even bismuth does not possess very marked metallic properties. Although metallic in appearance, it is a poor conductor compared to an element like copper; it is brittle and cannot be worked into sheets or drawn into wire; its hydroxide is by no means a strong base, even though it is stronger than the hydroxides of the other elements of the nitrogen group. Nor is bismuth a very good reducing agent. It is some-

what more active than the other elements of the group, but it does not reduce hydrogen ion to free hydrogen as do metals like sodium, magnesium or zinc.

Comparison of the metallic elements with one another would reveal the same type of difference in the degree of their metallic properties, although of course the differences are not so extreme as when metals and non-metals are compared. Nor do all of the metallic properties vary in the same order. Thus gold is a good electrical conductor, is very malleable and tenacious, but does not show decidedly positive (that is metallic) properties in its chemical behavior. These divergencies are noted more often amongst the elements of the inner than in those of the outer series. The reason is not known.

Table XXII gives a few of the physical properties of some of the more common metals. In many cases the results of different observers do not agree very closely. This is due to the fact that many metals are difficult to purify, and that their properties are greatly affected by small contaminations. The densities, unless otherwise stated, are those at 20° C., the boiling points those at 760 mm. The conductivities are given for 0° C. in most cases, and are expressed in terms of the reciprocals of the resistances (in ohms) of cubes with an edge of 1 cm. In comparing the conductivity data for the various metals it must be remembered that, since the densities of the metals vary widely, such cubes contain different weights of material. Thus although, in the units given in the table, copper has almost twice as great a conductivity as aluminium, weight for weight aluminium is the better conductor. All of the data have been rounded off to the nearest fairly reliable figure.

Occurrence of the Metals.—The less active metals are found free in nature, that is, in the **native** condition. Gold, silver, the metals of the platinum group, copper, mercury, bismuth, antimony and arsenic belong to this class. They are usually mixed with other mineral material. Some of these are found also in ores which contain oxides or sulfides, as for example, copper, mercury, arsenic, antimony, and bismuth. Other metallic elements, such as iron, manganese, tin, nickel, aluminium, and so on, are never found native but occur as oxides, sulfides, carbonates, or other

insoluble compounds. Silicates are very numerous, but as considerable difficulty attends the preparation of the metals from these salts, they are seldom used.

TABLE XXII

SOME PHYSICAL PROPERTIES OF THE MORE COMMON METALS

METAL	DENSITY, 20°	MELTING POINT, °C.	BOILING POINT, °C. (760 MM.)	CONDUCTIVITY, RECIPROCAL OHMS (0°)
Aluminium	2.71	658	1800	39
Antimony	6.62	630	1500	2.6
Barium	3.8	850	.....	.....
Bismuth	9.78	271	1420	0.9
Cadmium	8.65	321	767	1.3
Calcium	1.55	805	.....	.....
Chromium	6.92	1520	2200	38.5
Cobalt	8.7	1490	.....	10.3
Copper	8.93	1083	2300	64
Gold	19.27	1063	2500	45.5
Iron	7.80	1533	2450	10 (20°)
Lead	11.34	327	1525	5.0
Lithium	0.53	179	1400	11
Magnesium	1.74 (5°)	650	1120	23
Mercury	13.59 (4°)	38.89	357	1.0
Nickel	8.84	1452	.....	15
Platinum	21.41	1764	.....	9
Potassium	0.86	63	762	15
Silver	10.36	960	1950	67
Sodium	0.97	97.9	877	23
Tin	7.3 (15°)	231.9	2270	7.7
Tungsten	19	3200 (approx.)	.....	20
Zinc	6.92	419	905	17

Extraction of the Metals from their Ores.—Although different methods are employed for the production of the various metals from their ores, sufficient similarity exists between them to permit the making of a general survey. When the metal is native, the problem is one of removing the free metal from the adhering mineral material called gangue. In general, the metals melt at lower temperatures than the gangue, and a simple process of melting away the metal can be carried out. In other cases a flux

is added. The flux is a substance which interacts with the gangue to yield compounds of lower melting point. It is added to permit the separation of the gangue from the metal when both are molten; the denser metal sinks to the bottom, and separation is usually not difficult. Of course the details of the processes differ with different types of ore. **Metallurgy** is the branch of chemistry which deals with the extraction of the metals and their purification.

When the ore contains the metal as a compound, the latter is usually converted to the oxide, unless this is the compound present. Carbonates are converted into the oxides by heating, sulfides by roasting in air. The oxide is then reduced by carbon to the free metal. In many cases the actual reducing agent is probably carbon monoxide, formed by partial combustion of the carbon employed. None of these methods is satisfactory for the elements of the first two groups of the outer series, nor for aluminium; the special methods employed for them will be described later. On the small scale, metals are frequently prepared by heating the oxides with finely powdered aluminium which takes the oxygen from the other metal. A great deal of heat is evolved. The reaction has been used to mend broken metal parts, such as steel rails. The broken portion is covered with a mixture of iron oxide and aluminium powder, and the mixture lighted by means of a hot flame or a bit of burning magnesium ribbon. The molten iron formed in the reaction flows into the crack or break. The process is called **aluminothermy** or the thermite reaction.

Compounds of the Metallic Elements.—Most of the compounds of the metallic elements, especially those encountered in elementary work, are oxides, hydroxides or salts of various types. All of these are ionogens, and the simple types of reactions characteristic of ions therefore predominate in the chemistry of the metals. Two kinds of reactions need chiefly to be considered; (1) double decompositions and (2) reactions which involve oxidation and reduction. The behavior of the metals and their respective ions in reactions of the second type, determines the "activity" of the metals, and will be discussed in connection with the various groups as they occur in the periodic system. The principles underlying ionic double decompositions have already been taken up in considerable detail. Equilibrium in such reactions is determined by the degree of ionization and the solubility of the substances involved.

Although these matters are taken up in somewhat greater detail in later chapters, the following preliminary summary of degrees of ionization, solubilities and general methods of preparation will be of value in simplifying the remainder of the work.

Oxides.—The oxides are prepared most conveniently either by direct union of the elements, or by thermal decomposition of the hydroxides or of the salts of unstable oxygen acids, such as carbonates, nitrates, or sulfates. The more active the metal, the more readily it reacts with air or with oxygen, but the less easily do its hydroxides or salts decompose. Hydroxides are more easily decomposed by heat than nitrates, nitrates more easily than carbonates, and sulfates are the most stable of the compounds mentioned. Most of the oxides are very insoluble in all ordinary solvents.

Hydroxides.—The hydroxides of practically all of the metals, excepting those of the alkali and alkaline earth groups, are very insoluble in water. The insoluble hydroxides may be prepared by double decomposition of one of the soluble hydroxides and a salt of the metal. The hydroxides of the alkaline earth group metals are sufficiently insoluble to be prepared in a similar fashion by employing one of the alkali metal hydroxides. The fact that the hydroxides of the more active metals are the stronger bases has repeatedly been noted. (See Table X, page 201.) There are a few exceptions to the rule; thus, aluminium is one of the more active metals, but its hydroxide is a weak base. Some of the hydroxides are **amphoteric,** that is, they ionize either as bases or as acids. Of these, the hydroxides of aluminium, chromium, zinc, lead, antimony, arsenic, gold and platinum are the most common.

Salts.—A great many methods are available for the preparation of salts. Binary salts may often be obtained by direct union of the elements; salts containing more than two elements can usually not be obtained in this way. Other methods are (1) the neutralization of the acid furnishing the desired negative radical with the oxide [1] or the hydroxide of the metal, (2) treatment of a salt of a weak acid with a stronger acid, or (3) a double decomposition

[1] Many oxides, although basic in character, do not react readily with acids. This is most frequently true when the oxide has previously been heated to high temperatures. Thus aluminium and chromic oxides, after ignition, do not dissolve in acids. The reason for this is unknown.

in which the reaction is carried to completion by the precipitation or volatilization of some insoluble substance. Carbonates are particularly useful in making other salts because carbonic acid, being both slightly ionized and slightly soluble, is easily replaced by all but very weak acids. The exercises at the close of the chapter will provide material illustrative of these various methods.

Since all salts, with but very few exceptions, are highly ionized, most of their reactions are double decompositions or reactions of oxidation and reduction. The double decompositions are incomplete unless a slightly ionized or slightly soluble product is formed. The degrees of ionization of the various products which may be obtained in such reactions are found in the table on page 201; the solubilities of many of the common salts are contained in the table in the cover of the book. The following list of approximate solubility data is valuable.

TABLE XXIII

List of the Less Soluble Common Salts *

Halides.	All of the common halides except those of mercury (ous), silver and lead † are soluble. Chlorides are in general the most and iodides the least soluble of the slightly soluble salts. Fluorides cannot be classed with the other halides. Thus silver fluoride is quite soluble whereas many of the other fluorides are slightly soluble and a few (e.g., CaF_2) very insoluble.
Nitrates.	All nitrates are soluble. A few basic nitrates, like $BiONO_3$, and some nitrates of complex bases, not commonly encountered, are exceptions.
Sulfates.	The sulfates of barium, strontium and lead are very slightly, that of calcium somewhat more soluble.
Carbonates.	Practically all carbonates with the exception of those of the alkali metals are insoluble.
Other Salts.	Most **chromates** and **oxalates** are insoluble except for those of the alkali metals. The same statement applies to **phosphates, borates** and **silicates**. **Acid salts** are in many instances more soluble than the normal salts. **Permanganates** and acetates on the other hand are soluble with few exceptions (among which the silver salts may be mentioned).

It is to be noted that **none** of the common **salts of the alkali metals** is insoluble.

* Solubility in water only is under consideration. Most salts are much less soluble in non-aqueous solvents than in water.

† Lead chloride is slightly soluble in cold water and much more soluble in hot.

Alloys.—Materials consisting of two or more elements and possessing the characteristic physical properties of metals are called alloys. They are usually prepared by mixing molten metals and allowing the mixtures to cool. Other methods, however, are sometimes employed. When one of the components is mercury the special name, **amalgam,** is used. For convenience, the alloys may be grouped into three classes:

(1) Those in which the metals or other constituents are present as a heterogeneous mixture. As the molten mixture cools, crystals of one of the constituents deposit first. As cooling continues, a temperature is reached at which (assuming a binary mixture) the other also precipitates out. The crystals of the second metal are imbedded in a matrix of the first. This peculiar mechanical structure of alloys imparts to many of them the special character which makes them of value. When the alloy consists of more than two metals, the phenomena occurring on cooling may be analogous to those described, although somewhat more complex. The temperature and composition at which both metals crystallize simultaneously are called the eutectic temperature and composition respectively. (See page 140.)

(2) In some alloys the metals are present in the form of **solid solutions.** This means that each crystal, although perfectly homogeneous, contains a certain amount of each of the two metals and that all of the crystals, at least theoretically, are alike in composition.[1] Alloys of gold and platinum are of this type.

(3) In other types of alloys the metals unite with each other to form compounds.

The three types of alloys are not sharply distinguishable groups. The metals may be only partially soluble in one another; in that case at least two types of crystals are obtained. One of these consists of a saturated solution of the first metal in the second, and the other of a saturated solution of the second in the first. Similar phenomena occur with liquids. Thus when ether and water are mixed, the resulting mass separates into two layers;

[1] Perfect uniformity of the crystals is realized only if the melt is cooled so slowly that equilibrium is actually attained. Since the change involves solid material, it is very slow.

the upper one is a saturated solution of water in ether, the lower, a saturated solution of ether in water. Again, in alloys in which compound formation occurs, the compound may be mixed with or dissolved in an excess of one or the other of its constituents. It is obvious, therefore, that the study of alloys is a matter of considerable complexity. It is included in the large field called **metallography.**

The properties of alloys are in many instances markedly different from those of the component metals. In some cases the difference is due to the change in mechanical characteristics produced by the interlocking of the crystals; in other cases the lowering of vapor tension caused by the solution of the one metal in the other brings about a change of melting point and of other properties; in still other cases compound formation results in an entire change of properties. It is not known in all cases just how to account for the changes observed, because not infrequently minute additions of one metal to another cause relatively great alterations in properties. Thus steel, containing but 1 per cent of carbon, differs markedly from pure iron.

Alloys are of vast importance from the point of view of industry. Special steels and non-ferrous alloys are used in automobiles and aeroplanes; further mention of alloys and their uses is made in later chapters.

Intermetallic Compounds.—The compounds formed in many alloys are of unusual type, and of great interest from the point of view of the theory of compound formation, but they are as yet little understood. The metals are essentially positive elements, and have little tendency to form compounds by sharing of electrons. The compounds of metals with metals are therefore not accounted for by the theories which have been presented in this text. In these compounds the usual valences of the metals do not appear, as is shown by a few of their formulae: $NaZn_{12}$, $NaCd_5$, $NiZn_3$, etc. A second point of interest is that the intermetallic compounds, unlike those of the metals with typically negative elements, retain the physical properties of metals. It is probable that the forces leading to the union of the metals with one another are intermediate between those responsible for the formation of crystals and those responsible for the ordinary

type of compound—both being considered as different manifestations of the same fundamental property.

EXERCISES

(1) What differences are observed between the phenomena attending the passage of an electrical current through a metal and those attending its passage through a solution?

(2) If passage of electricity through a metal is accompanied by a drift of electrons, why is there no change in density at the two ends of the metallic conductor? In answering consider both the origin and the mass of the electrons.

(3) What are the physical characteristics of metals? Which of these may be directly related to the ease with which atoms of the metals lose electrons?

(4) What are the chemical characteristics of metals?

(5) Illustrate the gradual transition in properties from metals to non-metals.

(6) How might lead be obtained from lead sulfide? Copper from copper carbonate? Write the equations for the reactions involved.

(7) What is a flux? What is its function in metallurgy?

(8) Write equations for the preparation of metallic chromium from chromic oxide (Cr_2O_3) by aluminothermy.

(9) Suggest methods of preparation for the following compounds. In answering make sure that the method you suggest is one which involves only substances obtainable in a well supplied general laboratory: sodium sulfate, potassium nitrate, barium oxide, strontium hydroxide, zinc bromide, nickel sulfide, lead chloride. Write equations for all reactions.

(10) Define the terms: tenacity, ductility, malleability, elasticity.

(11) What is meant by the statement that antimonous hydroxide is more basic than acidic?

(12) In what respects do intermetallic compounds differ from the compounds of the metals with non-metals?

(13) What is an amalgam?

(14) In what way are the crystals of an alloy which consists of a mixture of two metals different from one in which the two metals form a solid solution?

(15) Name some of the alloys in common use, and describe how they are used.

REFERENCES

The reader is advised to consult the chapters on the individual metals for references on these elements and their compounds. The following books are very detailed, but will be found useful for special purposes.

H. Wysor—Metallurgy (1914). A book which describes the methods of extracting and purifying the most important metals. While not elementary, it is intended for the college student. It will be referred to again in connection with the individual metals.

C. Vickers—Metals and Their Alloys (1923) is somewhat similar in character but is addressed more particularly to engineers and others engaged in the metal industries. It contains a good chapter on the art of making alloys.

Jeffries and Archer—The Science of Metals (1924). A book covering the physics and chemistry of metals in general. An excellent book, but requires a good foundation in physics and the elements of atomic theory to be fully appreciated.

The two following books are standards in metallography. All of them presume that the reader is familiar at least with the elements of physical chemistry. The first is especially good from the point of view of the fundamental principles; the other gives more of the technique of the field.

Ruer—Elements of Metallography (translated by Mathewson) (1909).

Desch—Metallography (1910).

CHAPTER XXXII

THE ALKALI METALS

The first group of the periodic system consists of the metallic elements lithium, sodium, potassium, rubidium and caesium. Of these sodium is very plentiful, potassium occurs in many compounds, lithium is less common, while the last two are relatively rare. The usual source of sodium compounds is sodium chloride found in salt deposits, in salt wells, and in the oceans and salty seas. Potassium is found as the chloride (sylvite), and in various double salts of magnesium and potassium such as carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and schoenite ($MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$). The most extensive deposits are those of Stassfurt in Germany. Since potassium compounds are essential to plant life they must be supplied in the form of fertilizer to land which has been under active cultivation for some time. The Stassfurt salt deposits have been of very great commercial value. In this country during the war, there was great difficulty in supplying needed fertilizer material because the German supply was cut off. Potassium compounds occur in sea weeds (kelp) and in a variety of silicates. Partially successful efforts were made to prepare potassium compounds suitable as fertilizer from these sources, but the cost of most of the processes has been found too great for use in peace times. A method for using the potassium which occurs in the United States in the form of the silicates such as felspar and greensands has still to be found.[1]

Properties of the Group.—The elements of the group are very similar to each other in all respects. Only lithium, the first of the

[1] In the western part of the United States considerable quantities of readily available potassium compounds have been found in salt lakes and in deposits of alunite, $KAl_3(OH)_6(SO_4)_2$, and of leucite, $K_2Al_2(SiO_3)_4$. By-products from cement mills and sugar refineries also yield potassium salts.

group, shows marked departure in properties from the others. It is, in many respects to be pointed out later, more like a member of the second group than like an alkali group metal except, of course, for its valence and the formulae of its compounds. A similar phenomenon is exhibited by the properties of boron and of beryllium.

The alkali metals all possess a white metallic luster. This can be observed only at freshly cut surfaces, because the metals are so rapidly attacked by air and moisture that they become coated almost at once with a layer of hydroxide, which gives them first a bluish and then a dull whitish appearance. Their melting and boiling points are relatively low, as seen in Table XXIV.

TABLE XXIV

Melting Points, Boiling Points and Atomic Weights of the Alkali Metals

	Lithium	Sodium	Potassium	Rubidium	Caesium
Melting point...	186°	97.6°	62.5°	38.5°	28°
Boiling point....	1400°	877°	757°	696°	670°
Atomic weight...	6.94	23	39.1	85.44	132.8

The metals are so soft that they can readily be cut with an ordinary knife. This, of course, would be true also of other metals near their melting points; at very low temperatures the alkali metals display the mechanical properties characteristic of metals in general.

The outstanding properties of the group are the decidedly electropositive character of the elements, and the solubility of their compounds in water. These properties are illustrated by the methods of preparation of the elements, by their reactions and by those of their compounds.

Preparation of the Alkali Metals.—Very electropositive elements consist of atoms which readily lose electrons to form positive ions. These ions, on the other hand, do not easily regain the electrons to go back to the atomic condition; consequently it is very difficult to find any chemical reagent with which to reduce

the alkali metal ions to the free metals. Sodium and potassium have been prepared at high temperature by the action of carbon on the hydroxide:

$$6KOH + 2C \rightarrow 2K_2CO_3 + 3H_2 + 2K \qquad (1)$$

But the reaction is not at all satisfactory.

On account of the difficulty in preparing the elements by purely chemical means **electrochemical methods** have been applied to the problem. Under sufficiently high differences of potential, the ions of alkali metals can be forced to take on electrons. The reaction must of course be carried on in the absence of water, because the latter reacts violently with the free metals. To avoid this difficulty, fused sodium and potassium hydroxides are employed in the process, since they have relatively low melting points. In the course of electrolysis the metal and some hydrogen are liberated at the cathode, and oxygen and water at the anode. The two electrode compartments must therefore be separated to prevent interaction of the products. In the **Castner** process this is accomplished in a very simple manner. The molten sodium hydroxide is contained in a heated iron pot, Fig. 24, through the bottom of which the cathode *C* projects. This is held in

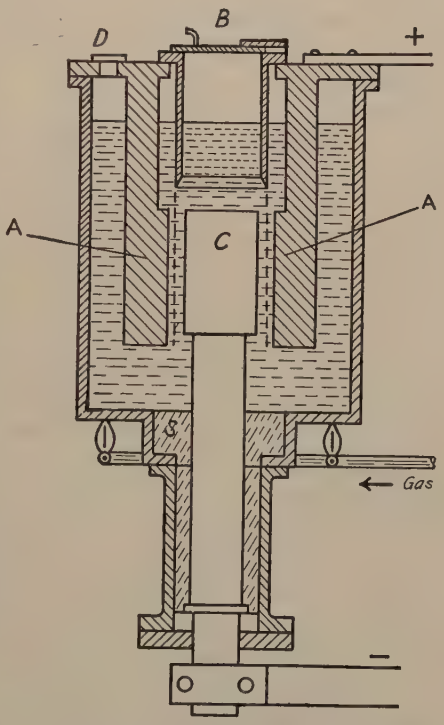


FIG. 24.

Taken from *Smith's College Chemistry* through the courtesy of the editor, Prof. J. Kendall, and the Century Company.

place by a cake of the solid sodium hydroxide *S*. The anodes *A* are suspended from above, so as to surround the cathode; but they are separated from it by a layer of the liquid and a cage of nickel gauze. A covered cylindrical vessel *B* of iron is supported in the fused hydroxide above the cathode. Since the free metal is lighter than the hydroxide, it rises to the top and collects in the cylinder. The hydrogen, which escapes through the opening in the top of the cylinder, protects the metal from oxidation by air. The oxygen escapes through an opening *D* in the pot, and at no time gets into the cylinder in which the metal is collected. From time to time, the latter is ladled out of the cylinder and poured into molds.

Sodium is the only one of the metals prepared in very large amounts, although metallic potassium is now also purchasable. Lithium may be prepared by electrolyzing a fused mixture of lithium and potassium chlorides, which melts at a lower temperature than either of the pure salts. But it is very difficult to obtain pure lithium in this way. Similar methods are used for the remaining elements of the group.

Chemical Properties of the Elements.—The free alkali metals react very readily with all of the decidedly electronegative elements. With the halogens the reactions are violent, and a great deal of heat is liberated. The reaction with oxygen takes place so easily that the metals must be protected from it, by submerging them in water-free kerosene or some similar liquid. The products formed in the interaction with oxygen are not the oxides, as might be expected, but the peroxides. (See page 90.) When potassium is exposed to air, the heat of the reaction with oxygen is sufficient to melt the metal and to set fire to objects near by. The same is probably true of caesium and rubidium.

As might be expected, the free elements are powerful reducing agents.[1] Thus they give up electrons to the hydrogen ions of water and acids, liberating free hydrogen. The reactions are violent. If large pieces of sodium are thrown into water, serious explosions may occur as a result of the ignition of the escaping hydrogen by the heat of the reaction; explosions result when even

[1] The actions of the metals with halides, oxygen, sulfur, etc., are illustrations of their reducing power.

very small amounts of potassium are used. Under suitable conditions the alkali metals displace all other metals from their salts, and reduce oxidizing agents such as nitric acid to the extreme products of reduction. In these reactions, precautions must be taken to prevent the reaction of the metals with the water, used as solvent, from becoming dangerously violent. This can be accomplished by using solutions of the metals in mercury (see sodium amalgam), which react more slowly than the pure metal. Thus sodium in sodium amalgam reduces copper sulfate to copper, and nitric acid to hydrogen and to ammonium nitrate.

Compounds of the Elements. Oxides and Hydroxides.— None of the usual methods for preparing oxides is applicable to this group. Treatment of the free metals with oxygen leads to the formation of peroxides; the hydroxides and the salts of oxygen acids are not decomposed to the oxides by heat. The oxides may be prepared by the action of the free metals on the hydroxides at high temperatures, or by heating the nitrates or nitrites with the free metals:

$$2KOH + 2K \rightarrow 2K_2O + H_2 \quad (2)$$

$$2KNO_3 + 10K \rightarrow 6K_2O + N_2 \quad (3)$$

No practical use has been discovered for the oxides. They react violently with water to give the hydroxides, and with oxygen to give the peroxides.

The **hydroxides** of sodium and potassium on the other hand are among the most important of reagents. Two general methods of preparation are to be considered. The first is an ionic double decomposition:

$$Ca(OH)_2 + Na_2CO_3 \rightleftarrows CaCO_3\downarrow + 2NaOH \quad (4)$$

Calcium carbonate is so much more insoluble than any of the other reacting substances that its precipitation determines the course of the reaction. It may be removed from the solution of the alkali hydroxide, dried, and converted into calcium oxide by heat. The latter is then allowed to react with water, and the resulting calcium hydroxide is used again.

With increasing availability of cheap electrical current, the method just described is gradually giving way to an electrochemical one. Electrolysis of an aqueous solution of sodium chloride leads

to the formation of sodium hydroxide at the cathode, and of chlorine at the anode. Unless separated from each other, these two products interact to form sodium hypochlorite at low temperatures, and sodium chlorate if the mixture is warm. A number of devices have been designed to avoid this difficulty.

The **Castner-Kellner** process, although not so much used as formerly, is of considerable interest because of its ingenuity. The electrolytic cell (Fig. 25) consists of three compartments separated by non-porous partitions which do not reach quite to the bottom. The bottom of the vessel is covered with mercury to a height sufficient to close the three compartments off from one another. A dilute solution of sodium or potassium hydroxide

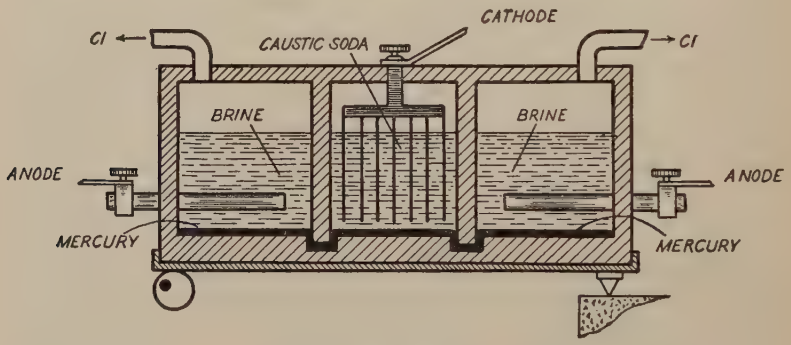


FIG. 25.

is then poured into the middle compartment, and a brine of the corresponding chloride into the two outer ones. The cathode, consisting of an iron grid, is immersed in the hydroxide solution; graphite anodes pass horizontally through the walls of the vessel into the brine. The current thus flows from the cathode through the hydroxide solution into the mercury, and from there through the brine to the anode. The mercury in contact with the brine is, therefore, more negative than the latter, and sodium or potassium ions are attracted to its surface and there discharged, forming a dilute amalgam. A rocking motion imparted to the cell causes the amalgam to flow from one compartment to the other. In the middle compartment, the amalgam is more positive than the solution with which it is in contact, and the potassium or sodium

of the amalgam is therefore reconverted into ions, which pass into the solution.

Simultaneously hydrogen is liberated at the cathode in the same cell, thus leaving the hydroxide ions of the water free to pair with the sodium or potassium ions. Chlorine is liberated from the brine in the outer compartment, and passes off as a gas.

At the present time, the **Nelson cell** is the most extensively used in the United States. In this device, Fig. 26, the vertical carbon anode is separated by the chloride solution and an asbestos diaphragm from a perforated steel cathode shaped like a wide test tube. The brine flows through the cell, and the sodium hydroxide solution produced penetrates through the asbestos and collects in a catch basin at the bottom of the apparatus. Chlorine escapes as a gas through an opening at the top.

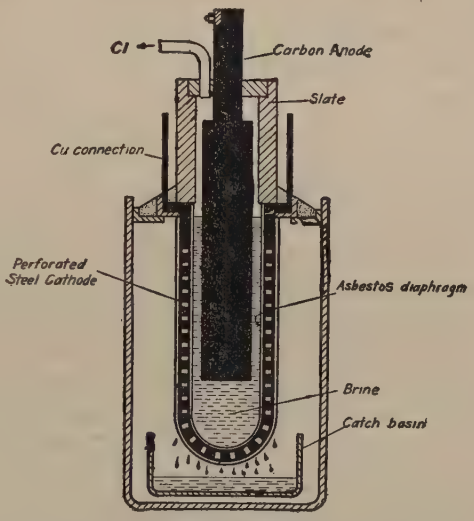


Fig. 26.

Taken from *Smith's College Chemistry* through the courtesy of the editor, Prof. J. Kendall, and the Century Company.

From the solutions obtained by any of these processes, the water may be removed by evaporation. During the evaporation the hydroxides melt, and the molten material is usually cast in sticks, or allowed to solidify in lumps and crushed. The hydroxides are extremely soluble in water, and are for this reason hygroscopic. They are very strong bases. Sodium and potassium hydroxide have been encountered so often in the preceding work that further description of their uses is unnecessary.

Carbonates and Bicarbonates.—The carbonates and bicarbonates, particularly of sodium, have been among the most important

reagents since the earliest days of chemistry. As salts of strong bases and a very weak acid, the carbonates of the group are decidedly alkaline, while the bicarbonates are but slightly so (see page 414). Furthermore, all but the weakest acids react with either the normal or the acid carbonates, displacing carbonic acid and liberating carbon dioxide. In this way these salts, although not so corrosive as strong bases, may be used to remove strong acids. Thus acids spilled upon clothes or the skin must not be neutralized with strong bases (which might be as harmful as the acids or worse), but may safely be removed by sodium bicarbonate. Its extensive use in medicine is likewise due to its action as a mild base.

The liberation of carbon dioxide from carbonates is itself useful, for example, in cooking. A dough, made with the addition of sodium bicarbonate and sour milk or a little vinegar, gives off bubbles of carbon dioxide during baking, and thus rises. The name **baking soda** is therefore given to sodium bicarbonate. When the use of vinegar or sour milk is undesirable, a **baking powder** is used. Baking powders are made by adding acid substances to the dry sodium bicarbonates. Alum, acid phosphates, or acid tartrates are the most common acid components. The bicarbonate and the acid substance do not react appreciably until the powder is moistened. It is desirable to use fairly insoluble acid material so that the reaction does not begin until the dough and baking powder have been thoroughly mixed.[1]

Another important use of the alkali carbonates is based on the fact that they are the only water-soluble carbonates. They are therefore employed in precipitating the carbonates of other metal ions from solutions. This type of reaction is important in the treatment of hard waters (see page 493) for use in boilers or laundries. The name, **washing soda,** for the hydrated sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, comes from the latter use. The uses of carbonates and bicarbonates in the preparation of other salts and of hydroxides have already been described.

Because of the many uses of sodium and potassium carbonates

[1] Commercial baking powders usually contain a little corn flour to keep the particles of the essential components separated and dry until they are mixed with the wet dough.

their manufacture has been a problem of very considerable importance. In the early days, potassium carbonate was extracted from wood ashes,[1] but at present it is manufactured chiefly by heating magnesite (magnesium carbonate) with potassium chloride in an atmosphere of carbon dioxide under pressure.[2] A number of processes for the manufacture of sodium carbonate have been devised. The first one used on the large scale was the Le Blanc process devised in 1791.[3] This has been almost completely displaced by the **Solvay or ammonia-soda** process invented in 1860. A solution of sodium chloride saturated with ammonia and heated to 40° is saturated with carbon dioxide. Two reactions occur:

$$NH_4OH + H_2CO_3 \rightleftarrows NH_4HCO_3 + H_2O \qquad (5a)$$

and

$$NH_4HCO_3 + NaCl \leftrightarrows NaHCO_3 + NH_4Cl \qquad (5b)$$

Advantage is here taken of the fact that the bicarbonates of the alkali metals (except lithium) are less soluble than the carbonates. The precipitated bicarbonate may then be heated to give the carbonate. Ammonium chloride, formed in the reaction, is reconverted into the hydroxide by heating it with lime. Pure sodium bicarbonate, for exacting chemical work or medicinal uses, is pre-

[1] This is the origin of the name "pot-ash."

[2] The reaction yields a hydrated double carbonate of magnesium and potassium ($2KHMg(CO_3)_2 \cdot 4H_2O$), and magnesium chloride. The former separates out in crystalline form while the latter remains in solution. The crystals are decomposed into insoluble magnesium carbonate and soluble potassium carbonate by heating with water at 120°.

[3] The reaction equations for this process are as follows:

Step 1: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
Step 2: $NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$
Step 3: $Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$
Step 4: $Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS$

The second step must be carried out at high temperature; the same is true of the third and fourth, which are usually simultaneous. The final mixture of sodium carbonate and calcium sulfide is leached with water, which dissolves the former. Calcium hydroxide is added to prevent hydrolysis of the sulfide. The process, although chemically rather simple, involves a number of relatively complex and slow mechanical steps, which need not be described, since the method is little used at present.

pared by dissolving the carbonate in water and saturating the solution with carbon dioxide, thus again precipitating the bicarbonate.

The ease with which the carbonates and bicarbonates are converted into each other is used in many ways. For example, a saturated solution of potassium carbonate at ordinary temperatures takes up carbon dioxide to form the bicarbonate. When the temperature is raised, the reverse reaction occurs, and carbon dioxide is again given off as a gas. This set of reactions is used for the purification of the gas.

Other Salts of the Alkali Metals.—The salts of the alkali metals, especially those of sodium and potassium, are extensively used because of their solubility and cheapness. In general sodium salts are the less expensive, but in some cases the potassium salts cost less since they are less soluble and therefore more easily purified by recrystallization. Many of the compounds have been in use since before the days of a scientific chemical nomenclature, and are still known by their old names. Thus the decahydrate of sodium sulfate, $Na_2SO_4 \cdot 10H_2O$, is still called Glauber's salt after the alchemist who first described its medicinal properties in the seventeenth century. The name " hypo " for sodium thiosulfate, used in photography, is an instance of an older name improperly used.

Many of these salts, such as sodium and potassium chlorides, nitrates, sulfates, and so on, are found in salt deposits of various kinds and are purified by recrystallization. Others are readily prepared by the general methods described in the chapter on the metallic elements. For some of them special methods are used. Descriptions of these methods are found in the more detailed reference books which may be used whenever need for detailed information arises. Attention has been called to several such works in the references cited in earlier chapters.

The salts of the alkali metals are relatively very stable. Thus the sulfates and carbonates are not decomposed into oxides by heat alone; the nitrates decompose into the nitrites, but not into oxides and nitric oxide, as do the nitrates of the less active metals. Even for such unstable compounds as chlorates and permanganates, the temperature necessary to effect decomposition is considerably higher for the alkali metal salts than for others. This stability

is unquestionably related to the decided electropositive character of the alkali metals. but the reason for the relationship is not a very obvious one.

Properties of the Ions of the Group.—The ions of the group are chemically inactive. The salts and hydroxides are highly ionized, which means that the positive ions of the alkali metal group have practically no tendency to unite with negative ions. The ions of the alkali metals take up electrons to become free metal with the greatest difficulty; they have therefore no oxidizing properties. Since the elements exhibit only the valence, one positive, and since their univalent positive ions are therefore unable to give up additional electrons, the ions possess no reducing action. The ions of alkali metals never enter into stable compound or complex ions. The only type of reaction, therefore, in which they take part is double decomposition. When these reactions go to completion the determining factor is usually some other ion. Thus the reaction between sodium chloride and silver nitrate is practically complete because silver chloride is insoluble, and that between sodium carbonate and an acid because carbonic acid is little ionized. In neither case is the presence of sodium ion a factor. If salts of the alkali metals are hydrolyzed it is because the acid from which the salt is derived is slightly ionized, and not because of any property of the alkali metal ions.

Very few of the salts of the metals of the group are insoluble. The only commonly used insoluble sodium salt is the pyroantimonate, $Na_2H_2Sb_2O_7$, which is employed in qualitative analysis for the identification of the element. Potassium forms only a few slightly soluble salts by means of which it may be identified. Among these are the perchlorate, $KClO_4$, the chloroplatinate, K_2PtCl_6, and the cobaltinitrite, $K_3Co(NO_2)_6$. Although relatively slightly soluble, these salts are much more soluble than such salts as silver chloride or barium sulfate. Lithium, however, differs from the other alkali group metals in this respect. Its carbonate, fluoride, phosphate, and quite a number of other salts are much less soluble than the corresponding salts of the other alkali metals, and are more like those of the alkaline earths.

The Hydrides of the Group.—All of the alkali metals react with hydrogen to form hydrides, of which NaH is a typical example.

Except in the case of lithium, the reaction takes place very slowly and incompletely at about 300°, while at slightly higher temperatures the hydrides again decompose. Lithium reacts very much more rapidly and completely, and its hydride is more stable than the others. In this respect again, lithium is like the alkaline earth group metals. The hydrides are moderately volatile, white, crystalline compounds possessing no metallic properties. They are very powerful reducing agents, and are inflammable in air. The most interesting fact about them is that, unlike hydrides of the non-metals, they are salts in which hydrogen is the negative ion. This has been demonstrated by showing that hydrogen travels to the positive electrode when the fused hydrides are electrolyzed.[1] Hydrogen is, of course, a fairly electropositive element, and when negatively charged, has an enormous tendency to give up 2 electrons to become ordinary hydrogen ion. This fact accounts for the great reducing power of the hydrides.

Amalgams and Alloys.—The alkali metals are soluble in mercury, forming amalgams. **Sodium amalgam** may be prepared by mixing the two metals, or by using a mercury cathode in the electrolysis of a solution of a sodium salt or of the hydroxide. When the amount of sodium in the amalgam is small the latter is liquid; with larger quantities of sodium the amalgam becomes solid. Sodium amalgam is used extensively as a reducing agent. Other alloys also may be formed. An alloy of sodium and potassium which is liquid at ordinary temperatures is occasionally used to remove the last traces of moisture or of oxygen from gases.

Similarity of Ammonium Ion to the Ions of the Alkali Metal Group.—Ammonium ion is in many respects similar to the ions of this group, especially to potassium ion. Its salts often crystallize in the same form; their solubility is very much like that of the potassium salts. Thus the perchlorate, the cobaltinitrite and the chloroplatinate are precipitated with those of potassium if both ions are present in solution. Ammonium salts must therefore always be removed by ignition before testing for potassium. The most striking similarity, however, is observed when a cold

[1] Thus far, the experiment has been carried out only with lithium hydride. The others are too unstable.

solution of ammonium chloride is electrolyzed with mercury as the cathode. The mercury swells up, turns dark, and gives off bubbles of hydrogen. A similar phenomenon is observed when sodium amalgam is treated with a very cold concentrated solution of ammonium chloride. The material reduces copper sulfate solutions to metallic copper just as does sodium amalgam, and reacts in many other ways as if it were an amalgam of the unstable substance ammonium, NH_4. Since only metals are soluble in each other, ammonium must be a compound metal with properties very much like those of the alkali metals. It differs from them in its instability, and in the fact that its hydroxide is a weak base

Spectra of the Elements.[1]—All elements have characteristic spectra which may be observed by examining with a spectroscope the light emitted by their glowing vapors. The spectra may be used to identify the elements or their compounds. The alkali metals and their chlorides are easily volatilized, and the spectra can therefore be observed without difficulty. The flame of a Bunsen burner turns yellow when a little sodium is introduced into it. When examined through a spectroscope, the light is seen to consist of two fine lines very close together in the yellow region of the spectrum. The violet color of the flame produced by potassium salts is due to the red and violet lines of the potassium spectrum. Each of the alkali metals or of their chlorides imparts to the flame a fairly characteristic color which may be used as a test for the elements; but the use of a spectroscope to study the exact composition of the light is far more reliable. Calcium, strontium and barium salts may also be identified by flame spectra. For most of the other metals this method is not applicable because the temperature of the flame is not high enough to volatilize them or their salts, or to excite the emission of the spectra. In such cases, solutions of the chloride are usually sprayed into a spark playing between platinum electrodes.

EXERCISES

(1) Make a tabular summary containing the following properties of the alkali metals: (*a*) characteristic physical properties; (*b*) chemical

[1] For detailed descriptions of spectra and of the instruments used in studying them text books of physics must be consulted. Any elementary book will give sufficient information for the present purpose.

properties of the elements; (*c*) characteristic chemical properties of the compounds of the elements (include the hydroxides, oxides and general characteristics of the salts).

(2) From the properties discussed in (1) select those which show the alkali metals to be the most decidedly electropositive of the elements.

(3) What are the chemical reactions involved in the Castner process for the manufacture of sodium?

(4) Write equations for the reactions of sodium or potassium with chlorine, with oxygen and with sulfur. By indicating the electronic changes in these reactions, show that they illustrate the behavior of the alkali metals as reducing agents.

(5) Why is the liberation of hydrogen from water by these elements also an illustration of their reducing action? Write the equations for the reaction.

(6) What is meant by the statement that reduction of nitric acid to ammonia represents extreme reduction of the former? Write the equation for a reaction in which sodium reduces nitric acid to ammonia (i.e., to ammonium nitrate).

(7) Write the equation for the action of sodium amalgam on copper sulfate solution. Note that mercury takes no part in the reaction.

(8) The reaction represented by equation (4), page 475, does not go quite to completion. Look up the solubilities of the substances involved, and explain why this is true.

(9) Why is sodium hydroxide formed at the cathode when an aqueous solution of sodium chloride is electrolyzed?

(10) What chemical changes occur in the Castner-Kellner process for the manufacture of sodium hydroxide?

(11) Explain why potassium carbonate is hygroscopic.

(12) Why do the acid materials and the sodium bicarbonate of baking powders fail to interact appreciably until the mixture is well moistened?

(13) Why does washing soda, which when fresh consists of clear crystals, become coated with a white powdery material on standing in dry air?

(14) The Solvay process for the manufacture of sodium carbonate involves only ionic double decompositions. What is the advantage of this over the Le Blanc process which involves reduction of sodium sulfate by carbon?

(15) Write the equations for the method of purifying carbon dioxide described on page 480.

(16) Suggest a series of reactions by which sodium carbonate could be prepared from sodium chloride. It is assumed that carbon dioxide and power in suitable form are available.

(17) Suggest a method for making sodium bromide from sodium hydroxide and bromine.

(18) Suggest a method for making sodium nitrate from sodium sulfate. It is assumed that any nitrate, other than that of sodium, and all acids are available.

(19) Suggest a method for making sodium fluoride. Calcium fluoride, any desired acid and sodium carbonate are supposed to be available.

(20) What is the evidence that hydrogen is the negative ion in lithium hydride?

(21) In what respects are "ammonium" and its compounds like the alkali metals and their compounds?

(22) In what respects is lithium more like an alkaline earth group element than an alkali group element?

(23) Write the equation for the reaction which probably occurs when sodium amalgam is treated with a solution of ammonium chloride.

REFERENCES

In the references to the preceding chapters the reader has been made acquainted with several works which can be used to find details about the elements and compounds still to be taken up. It is therefore considered unnecessary to refer in detail to such books as Lowry (Inorganic Chemistry); Friend (Text Book of Inorganic Chemistry); Mellor (Comprehensive Treatise) or the histories of chemistry. Even when no references are given the student should understand that one or the other of these books contains material which he can use. It should be remembered that the Lowry is more like a college text book, the Friend a reference book, and the Mellor a detailed treatise, but one which is so arranged that small sections of any subject are discussed independently. For this chapter the following special references are given:

Alembic Club Reprints—Number 6. Sir Humphry Davy, The Decomposition of the Fixed Alkalies and Alkaline Earths (1807–1808).

Stieglitz—Qualitative Chemical Analysis. Vol. II, page 12, gives a brief account of the use of the spectra of the elements in qualitative analysis. See also references to Chapter XXX, and those dealing with the manufacture of chlorine, hypochlorites and chlorates in Chapters XI and XXV of this text.

Martin, Smith and Milson—The Salt and Alkali Industry (1916). Like the other books by Martin referred to, this one gives in condensed form a considerable amount of information dealing with the manufacture of sodium sulfate and carbonate, and of potassium salts.

CHAPTER XXXIII

THE ALKALINE EARTH GROUP

The elements in the second group of the outer series of the periodic system are not so uniform in properties as are the members of the first group. Some writers place beryllium (also called glucinum) and magnesium with zinc, cadmium and mercury rather than with calcium, strontium, barium and radium. According to the Harkins arrangement of the periodic system, beryllium and magnesium fall clearly into the outer series as do the other alkaline earths,[1] whereas zinc, cadmium and mercury are inner series elements. Although beryllium and magnesium differ considerably from calcium, strontium, barium and radium, the differences are in general similar to those in other groups of the periodic system. Thus, beryllium is in many respects like aluminium. Its hydroxide is a moderately weak base which possesses acid properties, as does the hydroxide of aluminium, whereas the other hydroxides of the group are exclusively strong bases. This similarity between the first member of the group and an element of the succeeding group is not surprising—boron resembles silicon more than it does aluminium, and lithium resembles the alkaline earths more than the alkali metals. In outer groups the elements become more electropositive with ascending atomic weight; most of the differences between magnesium and the elements of higher atomic weight in the group may be associated with its less

[1] The term "alkaline earths" is usually reserved for the elements calcium, strontium and barium. The name is a very old one. Early chemists called very slightly soluble, non-metallic substances "earths." Some of these "earths" neutralized acids as do alkalies, and were therefore called "alkaline earths."

pronounced positive character or with the gradations characteristic of the group.[1]

Of the elements of the group only magnesium, calcium, strontium and barium are to be taken up in any detail. The important properties of radium were described in Chapter XXIII. Beryllium is also a rare element, although more abundant than radium; it is found chiefly in the minerals called beryls with the general formula $Be_3Al_2(SiO_3)_6$. Emerald is a hydrated beryl tinted green by traces of chromium compounds. The other elements of the group occur plentifully in various minerals. Magnesium is found chiefly as carbonate (magnesite) and silicates, of which talc and asbestos are familiar examples. Calcium is a constituent of a great number of minerals such as the carbonate (limestone, marble, chalk, etc.), a double carbonate of calcium and magnesium (dolomite), the sulfate (which occurs in the hydrated form as gypsum, $CaSO_4 \cdot 2H_2O$, the phosphate and various silicates. Barium is found chiefly as carbonate (witherite) or sulfate (heavy spar or barite). Strontium occurs as sulfate (celestite); it is the least common of the four.

Preparation of the Metals.—The alkaline earth group metals are prepared by electrolysis of the fused chlorides. The hydroxides cannot be used, as they decompose below their melting points into practically infusible oxides. Even the chlorides melt only at fairly high temperatures, so that considerable difficulty accompanies the manufacture of the metals. Magnesium is made in relatively large quantities by electrolysis of a mixture of magnesium, potassium and sodium chlorides or of carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$, which have lower melting points than the simple chloride. It is usually sold as wire, ribbon or powder and is used extensively for making "flash-light" powder and fireworks, because of the intense white light with which it burns. Calcium has only recently been put on the market; barium and strontium are not manufactured in large quantities.

[1] There is, of course, considerable justification for the placing of beryllium and magnesium with the zinc group just as there are certain advantages of placing it with the alkaline earths. Until a fundamental difference between the structure of inner and outer group atoms has been discovered, the question is one of classification chiefly.

Properties of the Metals.—All of the metals of the group have a silvery luster; they are harder, and have higher melting and boiling points than the alkali metals. They are very decidedly electropositive as shown by the ease with which they unite with negative elements such as the halogens, oxygen, sulfur, etc., and by their ability to displace hydrogen from water and from acids. Likewise they displace all other metals except those of the alkali group from solutions of their salts. Yet a very distinct gradation in positive character, of the type in accordance with their positions in the group, is readily observed. Magnesium is the least electropositive. It tarnishes relatively slowly in air, and reacts slowly with water at ordinary temperatures. Its hydroxide, like those of less active metals, is quite readily decomposed into the oxide. With increasing atomic weight the elements of the group become more electropositive; they react more rapidly with oxygen and with water, and their hydroxides become more stable. None of them, however, is as positive as are the alkali metals, for under suitable conditions [1] they are displaced by the latter. Moreover, the alkalies react more vigorously with water and oxygen, and form far more stable hydroxides and salts. The alkaline earth metals are almost as strong reducing agents as the alkali metals, as shown by the facts already mentioned and by their action on nitric acid with which they, like the alkali metals, yield ammonium nitrate and hydrogen. They share with but few other elements the ability of uniting directly with nitrogen to form nitrides (see page 289).

Oxides.—The oxides may be prepared by heating the hydroxides or the carbonates; the latter are more often used. The reaction for calcium oxide is:

$$\text{Heat} + \text{CaCO}_3 \rightleftarrows \text{CaO} + \text{CO}_2 \qquad (1)$$

When calcium carbonate is heated in a closed vessel, the reaction proceeds to the right until the pressure of the carbon dioxide reaches a definite value depending on the temperature. Application of Le Chatelier's rule leads to the conclusion that the

[1] When liquid ammonia is used as solvent, sodium and potassium displace barium and other alkali metals from solutions of their salts.

higher the temperature the farther the progress of the reaction to the right, and the higher the equilibrium pressure of the carbon dioxide. It is clear that decreasing the partial pressure of the gas (either by enlarging the vessel or by diluting the carbon dioxide with some indifferent gas) must also cause the reaction to go further to the right, and that increasing the carbon dioxide pressure must have the opposite effect. To secure the maximum yield of calcium oxide it is, therefore, desirable to use a high temperature and to remove the carbon dioxide as rapidly as possible by means of a good draft. But it is possible to overheat the material. The calcium carbonate used for the manufacture of calcium oxide on the large scale is not pure; the siliceous material usually present reacts with the oxide to give silicates. These fuse at high temperatures, and thus coat the pores of the product, rendering it inactive. For these reasons the kilns, in which the oxide is made, are so constructed that the raw material does not come into contact with the solid fuel, but is heated by the flames and hot gases from the fire.

The principles which apply to the manufacture of the other oxides of the group are no different from those applying to calcium oxide. The partial pressure of carbon dioxide in equilibrium with the respective oxides and carbonates at any given temperature is, however, different for each of the substances; it is highest for magnesium carbonate and lowest for barium carbonate. In other words, the highest temperature is required for efficient manufacture of barium oxide, and the lowest for magnesium oxide. For the former the temperature is so high that carbon is often added to aid in the removal of carbon dioxide and in the production of heat:

$$BaCO_3 + C \rightarrow BaO + 2CO \qquad (2)$$

The oxides are white solids of very high melting points and great stability.

The differences in the properties of the oxides lead to different uses for them. Magnesium oxide, commercially known as calcined magnesia,[1] reacts very slowly with water especially if it has been

[1] The ending "a" is often used to designate oxides as in magnesia, MgO,

prepared from the carbonate at high temperatures. It is very infusible and a poor conductor of heat. On account of these properties it is used as a lining for electric furnaces, and as insulation on steam pipes and boilers to reduce heat losses. The most important uses of calcium oxide, on the other hand, depend upon the fact that it reacts readily with water. Thus, in making **mortar,** the oxide (burned lime) is first mixed with about twice the amount of water required to convert it into the hydroxide (slaked lime); to the thick paste are added 2.5 to 3 volumes of sand and enough additional water to give the mass the right consistency. The setting of mortar is due to the loss of excess water and to the interaction of the calcium hydroxide with carbon dioxide of the air. The crystalline calcium carbonate formed is interlaced with the sand, thus giving a rigid porous structure which adheres to brick or stone. Only the surface of the mortar reacts quickly with carbon dioxide; during the first year the reaction proceeds to a depth of only about 2.5 mm., and complete conversion of a normally thick layer of mortar into carbonate is said to take over twenty years. If it were not for the porosity of its structure, the mortar would probably receive only a coating of carbonate, and would be much less firm and adhering.

Although barium oxide also reacts very readily with water its particular usefulness depends upon an entirely different property. Barium oxide resembles the oxides of the alkali metals in its reaction with oxygen to form the peroxide:

$$2BaO + O_2 \rightleftarrows 2BaO_2 \qquad (3)$$

Action toward the right takes place at moderately high temperatures when air under pressure is passed over the oxide. By evacuating the apparatus and thus decreasing the partial pressure of the oxygen, the reaction is reversed, and oxygen is again liberated. **Brin's process** for obtaining oxygen from air is based upon this reaction, but it has been largely displaced by the other methods mentioned in Chapter VII. Barium peroxide is, how-

silica, SiO_2, etc. But the ending is used in other ways also, as in washing soda, $Na_2CO_3 \cdot 10H_2O$, and is therefore best avoided.

ever, still extensively used in the manufacture of hydrogen peroxide.[1]

The Hydroxides.—The hydroxides of the group may be prepared by treatment of the oxides with water. They may also be precipitated from solutions of the alkaline earth salts by soluble highly ionized bases such as sodium hydroxide. Barium and strontium hydroxides crystallize from aqueous solutions as hydrates with 8 molecules of water. Barium hydroxide, which is fusible without extensive decomposition, is the most stable of the group, and magnesium hydroxide the least stable. The solubility varies in the same order, barium hydroxide being the most soluble.[2] Because of the cheapness of calcium hydroxide it is extensively used in industry in almost all reactions requiring a base. It is not very soluble in water, but a mixture of the solid hydroxide and its saturated aqueous solution may be used; as soon as the dissolved material reacts, more of the solid goes into solution, thus maintaining the concentration of hydroxide ions high enough for many reactions. Although not so active as the bases of the first group, the hydroxides of the alkaline earths belong to the strong bases. Their salts of strong acids are therefore not hydrolyzed; those of the weaker acids are hydrolyzed to only a moderate extent.

Properties of the Ions of the Group. Solubility of the Salts.—The alkaline earth metals are so electropositive that the electrons lost in the formation of the ions are not readily regained. For this reason the ions do not act as oxidizing agents. Nor can they be reducing agents because the only valence of these elements is 2+, and the ions are therefore unable to give off further electrons. All of the common compounds, that is, the

[1] It is interesting to note the relationship between the electropositive character of the elements and their ability to form peroxides by direct union of the oxide with oxygen. In the alkaline earth group only the oxide of barium, the most electropositive element, has this property, and the peroxide is relatively easily decomposed. The oxides of all of the alkali metals, which are decidedly more electropositive than barium, unite with oxygen to form very stable peroxides.

[2] For the position of radium hydroxide in this series, see page 331. An interesting fact about calcium hydroxide is that its solubility decreases with rise in temperature.

salts and hydroxides, are highly ionized, so that double decompositions are the chief type of reaction; hence the solubility of the salts taking part in them determines the direction in which such reactions proceed.[1] A large proportion of the salts of this group are slightly soluble in water (see the table of solubilities and the summary on page 466). In many instances regularities in solubility, like that of the hydroxides, are found in the case of the salts. Thus barium sulfate is the least soluble of the sulfates, and magnesium sulfate the most soluble, while the others fall into the list in the order of their atomic weights.

Hydrides.—The metals of the group, except magnesium and beryllium,[2] unite readily with hydrogen at temperatures from 300° to 500° with the evolution of a considerable amount of heat; the hydrides thus formed are moderately stable. The alkaline earth metals are therefore like lithium in their behavior toward hydrogen, and unlike the rest of the alkali group metals; the hydrogen in all of these hydrides, however, seems to function as the negative ion.

Hardness of Water.—Water which contains in solution salts of this group, especially of magnesium and calcium, is known as **hard water.** Most natural waters are more or less hard because of the prevalence of these salts in the soils through which the water percolates. Hard water leaves behind what is known as **boiler scale** when it is evaporated in the tubes of boilers, and thus causes great fuel waste because transfer of heat from the fire to the water is partially interrupted. Hard water is also objectionable in the laundry. Soaps are sodium or potassium salts of long chain organic acids which react with soluble magnesium or calcium salts to form the very slightly soluble magnesium or calcium soaps. On this account, hard water causes the precipitation of the effective emulsifying agent of the

[1] Except, of course, when one of the salts in question is derived from a weak acid. In that case, displacement of the acid by a stronger one may be the directing influence. It is obvious that, in considering the properties of a salt, the characteristics of the negative ion must be considered. An iodide of the alkaline earth group has all of the properties characteristic of iodides in general, and so on.

[2] In their failure to form hydrides, beryllium and magnesium are more like inner group elements than like those of the outer groups.

soap. Of course if enough ordinary soap is added to the water all of the hardness is removed. Such a proceeding is not only objectionable from the point of view of economy, but also because the calcium or magnesium compounds are precipitated as slimy deposits which are difficult to remove.

In planning methods for the removal of hardness from water, the nature of the dissolved salts must be considered. Calcium carbonate is one of the most common constituents of soils and rocks over which water passes. The carbonate itself is too insoluble to affect the water, but it reacts with dissolved carbon dioxide to form the soluble bicarbonate:

$$CaCO_3 + H_2O + CO_2 \rightleftarrows Ca(HCO_3)_2 \qquad (4)$$

The reaction is reversible. Consequently, removal of carbon dioxide, which occurs when the water is boiled, drives the reaction to the left, and removes calcium ion by precipitation of the carbonate. Such hardness, known as **temporary hardness,** can therefore easily be overcome. For boiler use, however, water with temporary hardness is just as objectionable as water which contains salts not precipitable by boiling (**permanent hardness**), for it is not feasible to boil and filter or settle large amounts of water for factory use. The acid salt, responsible for temporary hardness, may be removed by neutralizing the hydrogen ion. For this purpose slaked lime is used, as it is cheap and precipitates all of the calcium as carbonate.

Permanent hardness may be caused by any of the soluble salts such as sulfates of the two metals most commonly involved. In this case sodium carbonate may be used to overcome the hardness, for it precipitates the insoluble carbonates and leaves unobjectionable sodium ion in their place. Hence, sodium carbonate is extensively used in the household, as is borax, which also forms insoluble calcium and magnesium salts by double decomposition. Ammonia neutralizes the hydrogen ion of bicarbonates; it also unites with carbon dioxide in the water to form ammonium carbonate, which removes other calcium salts. Ammonia, however, does not precipitate magnesium salts. Sodium carbonate and borax, when added to water,

also remove soluble iron salts and thus prevent the staining of clothes with rust.

A very important method extensively used in industry for softening water is the **permutite** process. Sodium silico-aluminate (permutite) is an insoluble substance which reacts with calcium and magnesium salts to give insoluble calcium and magnesium permutites. Writing for the complex negative radical the symbol Pe, gives the simplified equation:

$$CaSO_4 + 2NaPe \rightleftarrows CaPe_2 + Na_2SO_4 \qquad (5a)$$

The reaction is reversible; therefore treatment of the calcium permutite with a large excess of a sodium salt reconverts the material into the sodium compound. If sodium chloride is used, the reaction is:

$$2NaCl + CaPe_2 \rightleftarrows 2NaPe + CaCl_2 \qquad (5b)$$

The calcium chloride is washed away, and the permutite used over again. The latter is used in coarse, sandy form so that the water may simply be filtered through it.

Uses of the Compounds of the Group.—A great many uses of the various compounds of this group have already been mentioned in this and other chapters. Among important products containing calcium compounds are cyanamide, bleaching powder, glass, porcelain, enamels, cement, mortar, lime, limestone and others. These have already been discussed. Calcium phosphate is a mineral widely used in making fertilizers. It is first converted into an acid phosphate, $CaH_4(PO_4)_2$, which is more soluble than the normal phosphate and therefore a better source of phosphorus for plants. Plaster of Paris, $(CaSO_4)_2 \cdot H_2O$, owes its usefulness to the fact that when it unites with water to form gypsum, the mass swells and fills out every detail of the mold into which the mixture of the plaster and water has been poured. Calcium chloride unites with water to form a hydrate of very low aqueous tension; the anhydrous salt is therefore an excellent drying agent, as is also the bromide.[1] Magnesium salts are used

[1] Calcium chloride and bromide unite also with ammonia to form compounds similar to the hydrates.

in medicine; barium sulfate as a white pigment in paints,[1] and in filling glazed paper and cards. Both barium and strontium salts are used in making colored lights and fireworks. The former produces the green and the latter the red variety.

Comparison of the Alkaline Earth and Alkali Metal Groups.— Review of this and the preceding chapters should make clear that the alkaline earth and alkali metal groups are similar in very many respects. Both consist of very electropositive elements, which are very reactive toward all electronegative elements, toward water and toward acids. They are powerful reducing agents. For reasons already given, the ions of both groups are relatively inactive. The groups nevertheless show distinctive differences. The valence of all of the elements of the first group is 1 +, of those of the second group, 2 +; the second group is not so uniform as the first; in the first group there is a much smaller number of slightly soluble salts. The elements of the first group are more electropositive. Instances of this fact have been noted in various sections of this chapter, but one other may be cited. The carbonates of the first group are not decomposed by heat at any temperatures yet attained; the nitrates are decomposed only to nitrites. The carbonates of the second group are decomposed at moderately high temperature; the nitrates decompose to nitrites at moderately high temperatures, but decompose further into oxides when heated strongly. Other similarities and differences have been described in connection with the discussion of the elements and the various compounds; making a summary of them will afford an excellent review of the two chapters.

EXERCISES

(1) (*a*) In what respects are beryllium and its compounds different from the characteristic elements of the group? (*b*) Answer the same question for magnesium and its compounds. Show how the differences in each case are, in part, of the type to be expected by analogy with other groups of the periodic system.

[1] Lithopone is a mixture of barium sulfate and zinc sulfate, and is a pigment of great covering power. It has the advantage that it does not darken by interaction with hydrogen sulfide as does white lead.

(2) Assuming that magnesium is the only product formed at the cathode during electrolysis of fused magnesium chloride, calculate how much of the metal should be liberated by the passage of a current of 4 ampères flowing for 10 hours.

(3) What properties of the elements of the group show the increase in electropositive character with ascending atomic weight?

(4) Predict what should be the properties of barium sulfide. Suggest two methods for its preparation.

(5) Explain why impure magnesium oxide, prepared by burning magnesium in air, gives ammonia when it is treated with water.

(6) Account for the differences in the uses to which magnesium oxide, calcium oxide, and barium oxide are put.

(7) Give an equation for the preparation of hydrogen peroxide from barium peroxide.

(8) Is heat given out or absorbed when calcium hydroxide dissolves in water? (See footnote 2, page 491.)

(9) Would you expect radium sulfate to be more or less soluble than barium sulfate? Why?

(10) (*a*) What type of evidence should be sought to determine whether hydrogen acts as the negative ion in calcium hydride? (*b*) What properties might be predicted for calcium hydride?

(11) (*a*) Why is hard water objectionable? (*b*) How does borax remove hardness from water? (*c*) In the permutite process, what is the only substance actually consumed in removing hardness? (*d*) In preparing water for household laundry purposes, should the washing soda or borax be added before or after the soap? (*e*) What is the objection to the use of these substances?

(12) Make a tabular comparison of the alkali metal and the alkaline earth metal groups of elements, including important compounds as well as the elements themselves. In addition to the table, make a statement in which the differences and similarities are summarized.

REFERENCES

See note on References at the end of the preceding chapter, and the References to Chapter XXX.

Water softening is described in Rogers, Industrial Chemistry, pages 86–95.

CHAPTER XXXIV

THE COPPER GROUP

Complex Ions.—Double Salts.—Equilibrium in Reactions of Oxidation and Reduction

The copper group, consisting of copper, silver and gold, is the first group of the inner series taken up in this text. In the discussion of its properties a number of very striking differences between it and the main, or outer, groups will be brought out. It is impossible, however, to make as many general statements about the inner groups as about the outer ones. A large number of the elements of these groups are relatively rare and not thoroughly investigated; even for some of the more abundant many fundamental data are still lacking. The inner groups are far less uniform than the outer ones; and their elements form a large number of very complex compounds of uncertain structure. As yet none of the hypotheses of atomic structure, valence, and compound formation accounts satisfactorily for the properties of these elements. It is therefore necessary to treat the members of most of the inner groups individually rather than as members of fairly coherent families, and often only a few facts are known with certainty. On this account, most of the inner group elements receive but scanty attention in text books of general chemistry. This neglect must, however, not lead to the false notion that the inner group elements are of little importance. Many of them are of considerable practical value. Furthermore, it is essential that they be investigated further, for the very fact that their behavior and relationships to other elements are so little understood is evidence of the incompleteness of our present theories.

Occurrence and Metallurgy of the Copper Group.—All of the metals of the copper group occur free in nature. This in

itself proves that they are far less reactive than the metals which have been discussed in the preceding chapters. Copper occurs also in large deposits as sulfide, as chalcopyrite, $CuFeS_2$, as basic carbonates (malachite, $Cu_2(OH)_2CO_3$, or azurite, $Cu_3(OH)_2(CO_3)_2$) and as cuprite, Cu_2O. Silver, too, is found in compounds, such as sulfides and chlorides; with gold this is less commonly the case. Gold and silver are frequently alloyed with each other in their ores; they both are usually present in copper ores and sometimes in those of lead and of mercury.

The manufacture of **copper** from the ores in which it occurs free is relatively simple, for the metal may be separated by washing from the mineral matter, to which it is attached. It is then purified by being smelted with a flux. To obtain the free metal from sulfide ores is more difficult both because these ores are not readily reduced, and because they contain a large amount of iron. The process usually employed is quite complex; it may be outlined briefly as consisting of three steps. In the first, the ore is roasted to remove most of the volatile impurities. During this process the sulfides are partly oxidized. Iron oxide [1] thus formed combines with silica (either present in the original ore or added during the roasting), and constitutes a fusible slag which may be removed from the ore. The function of the second step, carried out in a blast furnace, is to convert the partially oxidized and purified material into a mixture of cuprous and ferrous sulfides, called **copper matte.** This is accomplished by heating the product from the first step with some of the untreated ore and with silica, which removes more of the iron oxide as described above. The third step is carried out in a Bessemer converter. This is a device in which the highly heated melted matte is oxidized by forcing compressed air through it. The vessel is lined with siliceous material with which iron oxide, obtained in this step by complete oxidation of the sulfide, reacts to form a slag; at the same time cuprous sulfide is partially oxidized to the oxide. The oxide and unchanged sulfide react to form copper:

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \qquad (1)$$

[1] In a mixture of copper and iron sulfides, the latter is oxidized by air before the former is attacked.

The equation, however, represents only one of a number of reactions which are supposed to take place in the manufacture of copper.

The processes by which **silver** is extracted depend largely on the nature of the ores. The sulfide, for example, may be converted by roasting into the sulfate which is soluble in water. Silver is readily precipitated from the aqueous solution obtained. If the ore contains silver as chloride, treatment with mercury is effective:

$$AgCl + Hg \rightarrow Ag + HgCl \qquad (2)$$

The silver amalgamates with the excess of mercury and the latter is removed from the amalgam by volatilization. **Parke's process** of separating silver from lead is not only commercially important, but is of interest because it illustrates the application to molten metals of a process often employed with liquids at ordinary temperatures. The process in question is analogous to the extraction of iodine from water by means of ether. When ether is shaken with an aqueous solution of iodine, the latter, which is more soluble in ether than in water, dissolves in the ether and rises with it to the upper layer. Silver is more soluble in zinc than in lead, and the two last named metals are not very soluble in each other. When zinc is mixed mechanically with molten lead containing silver, the lighter zinc ultimately rises to the top, carrying with it most of the silver and very little lead.[1] The zinc is then distilled off, and silver containing traces of lead is left. The small amount of lead is removed by converting it into a fusible oxide (cupellation).

Gold is found chiefly as free metal. If the ore is rich, mechanical separation of gangue and metal is employed, as in placer and in hydraulic mining. Poorer ores and the residues from rich ores require chemical treatment. The most common method is to dissolve the gold in potassium cyanide, and to reprecipitate it from solution by zinc.[2]

Extraction of the metals from the ores is usually preceded by a process of concentrating the ore to remove material con-

[1] Most of the silver is present in the zinc solution as the compound Ag_2Zn_5.

[2] The action of gold with potassium cyanide is a complex chemical reaction, and not a simple process of solution.

taining no metal or metallic compounds. Washing or other mechanical methods are used. The flotation process for concentrating copper ores was touched upon in the chapter on colloids (page 446).

Refining of Copper.—Many of the uses to which the metals of this group are put require a high degree of purity which, especially in the case of copper, is not attained by the process of extraction. Several methods for further purification are used. Of these, the electrolytic one is of especial interest. Impure copper is cast into slabs which are made the anodes in a bath of copper sulfate acidified with a little sulfuric acid. Between the anodes and very close to them a series of cathode plates, made of pure copper, are placed. A certain voltage between the plates is necessary to cause the copper to go into solution as copper ions. This voltage is sufficient also to dissolve metals more active than copper such as zinc. But if the minimum voltage necessary to dissolve copper is not overstepped, less active metals such as silver and gold do not dissolve. As the copper is worn away by conversion into ions, the silver, gold and other undissolved impurities fall to the bottom of the vessel. They are collected and furnish a number of valuable products. At the cathode the reverse process occurs. If the voltage is just high enough to deposit metallic copper, it is also high enough to deposit the less active metals. But the latter have not gone into solution and can therefore not contaminate the copper. The minimum voltage required to deposit copper is not high enough to deposit the more active metals. By careful regulation of the voltage and other factors, such as concentration of acid, temperature and current density, it is thus possible to secure a deposit of copper which is 99.95 per cent pure or even purer.

Electroplating.—Processes similar to that described for the refining of copper may be used to deposit metals upon one another. The more active elements, like iron, are frequently plated with the less active ones as a protection against corrosion. Plating iron with nickel or with copper, or steel with silver are familiar examples. The metal to be plated is made the cathode, and the metal to be deposited the anode. In plating

with a metal which, like gold, is difficult to dissolve, a solution of ions of the metal and an inactive anode such as platinum may be used. Although the principle of electroplating is thus quite simple, successful results depend upon a great many details. In order to obtain a well-adhering deposit the voltage, strength of the current, and other factors must be carefully controlled, and the nature of the solution employed as electrolyte is of great importance.

It is possible also to deposit metals on non-metallic objects. The surface of the object is first rubbed with graphite to make it a conductor. It may then be used as cathode in the manner described for ordinary plating. **Electrotyping** is an application of this method. A cast is made of a page of type. The cast is coated with copper by electrolytic deposition, and then stripped off. Next, it is strengthened by filling the back with molten lead or stereotype metal, an alloy of lead, antimony and tin.

Properties of the Metals.—The elements of the group possess to a marked degree the physical properties of metals. They are among the best conductors of electricity, they are very ductile and malleable. The melting points are not very high. These properties, and their resistance to corrosion, have led to a great variety of uses too well known to warrant further description. Attention may be called to the lack of uniformity in the color of the elements in massive form; copper is red, silver white, and gold yellow. The colors of colloidal suspensions depend on the sizes of the colloid particles. Colloidal gold suspensions vary in color from blue to red.

The elements exhibit very marked differences in chemical properties. Copper has the greatest tendency to go into the ionic condition, gold the least. Thus copper, when finely divided, burns in an atmosphere of chlorine, and unites readily with the other halogens and with sulfur; silver reacts much more slowly with these elements; gold acts with the halogens slowly and only at slightly elevated temperatures; it does not act at all with sulfur. Copper is slowly attacked by oxygen particularly in the presence of carbon dioxide. The beautiful patinas which coat old copper roofs are due to the formation of a basic copper carbonate. Silver is not oxidized by oxygen at

ordinary temperatures; it tarnishes only because of the presence of sulfur compounds, such as hydrogen sulfide, which coat it with a thin layer of silver sulfide. Gold is not affected by oxygen or hydrogen sulfide. The same gradation in properties is shown by the metals in their behavior toward oxidizing agents. None of them reacts with water or with hydrogen ion of acids as do the alkali or alkaline earth group metals. Copper acts with dilute nitric acid to give nitric oxide; the primary reduction product of the acid by silver is nitrogen tetroxide, while gold does not act at all.[1] This difference in action toward nitric acid is used in the commercial separation of gold and silver.

In agreement with the order of activity demonstrated by these reactions, copper displaces silver from solutions of its salts, and silver displaces gold. Conversely, cupric ions show the smallest tendency to revert to the free metals. Nevertheless cupric ions quite readily take up electrons to become metallic copper, as shown by their ability to act as moderately strong oxidizing agents. Thus copper is displaced from its salts by a large number of more active metals. Copper ion solutions act as oxidizing agents in other reactions also, as for example in the action of Fehling's solution [2] on glucose and other aldehydes, but in many of these reactions the change from cupric to cuprous ion, to be discussed below, is an important factor. Silver ions are stronger oxidizing agents than copper ions, and gold ions have the greatest oxidizing power.

Two marked differences between this group and the alkali metal and alkaline earth metal groups are therefore to be noted. In the copper group electropositive character becomes less pronounced with increase in atomic weight whereas in all outer groups the reverse is the case. In the second place the elements of the copper group are much less electropositive than the alkali or alkaline earth group metals. This is shown by displacement reactions and by the much smaller reducing power of the copper group elements. Moreover, the ions of the outer group elements under discussion have no oxidizing power,

[1] Details of the action of nitric acid on copper and silver and the action of gold on aqua regia have been discussed on pages 317, 319, and 321.

[2] See page 515.

whereas the ions of the copper group easily take up electrons to become free metals.[1] The discussion of the properties of compounds of the copper group will illustrate these differences further.

Passive Copper.—The statements made above concerning the action of copper on air and on acids referred to copper in its ordinary condition. But copper is subject to certain changes which greatly alter its activity. An ordinary copper rod is rapidly attacked by nitric acid of specific gravity 1.4, but if the rod is brought into contact with a piece of platinum the action of the acid is checked. After removal of the platinum, the copper remains in its inactive condition. The same condition is produced by dipping the copper into stronger nitric acid (sp. gr. 1.5). The difference between the inactive, or as it is called, the **passive** copper and ordinary copper is shown by dipping a strip of each into a 0.1 per cent solution of silver nitrate. The ordinary copper becomes immediately coated with a grey deposit of silver, while the passive sample remains bright for several minutes.

Other metals besides copper exhibit similar phenomena. A particularly striking experiment may be carried out with iron which becomes passive when dipped into fuming nitric acid. The passive iron may be dipped into a solution of copper sulfate without becoming coated with the usual red deposit of copper; but if the piece of iron is sharply struck, it at once becomes active, and is immediately covered with copper. No satisfactory explanation of the phenomenon is known. The inconsistencies found in statements concerning the reactivity of copper, towards air for example, may be due to partial persistence of a passive condition; but they may also be due to differences in fineness of division of the copper used by different investigators,

[1] Students frequently confuse properties of the free metals with those of the ions of the metals. In general, a metal which has a pronounced tendency to go into the ionic condition by losing electrons forms ions which have very little tendency to take on electrons and to revert to the metallic condition. In other words, metals which are powerful reducing agents form ions which have no oxidizing properties while the metals which are poor reducing agents form ions which are oxidizing agents.

or to the presence of coatings of various sorts on the surface of the copper.

Valence of the Elements of the Group.—Copper forms cuprous compounds in which its valence is one positive and cupric compounds in which it is two positive; silver is one positive in all of its compounds; gold is one positive in aurous and three positive in auric compounds. This variety is in decided contrast to the uniformity of valence in the alkali metal and alkaline earth groups. All of the elements of the copper group, however, are 1+ in some of their compounds, and are thus characterized as belonging to the first sub-group. In making comparisons of the compounds of the elements the differences in valence must be considered. Cuprous and cupric ions are entirely different substances, as are also aurous and auric ions. A logical comparison must, therefore, be limited to compounds in which the elements display the same valence.

The Oxides and Hydroxides.—The oxides of copper may be prepared by the action of copper on air or on oxygen, but are obtained most readily from other copper compounds. **Cuprous oxide,** Cu_2O, is precipitated as a reddish-yellow powder by reduction of cupric salts. The action of glucose on Fehling's solution is an illustration. In many of the reactions, the oxide is obtained in hydrated form. Black cupric oxide, CuO, is easily prepared by heating cupric hydroxide. Both oxides decompose into oxygen and the free metal when heated to high temperatures.

Silver oxide and the **two oxides of gold,** Au_2O and Au_2O_3, are prepared by treating the corresponding salts with some base, and allowing the resulting precipitates to dry. Silver oxide decomposes readily at moderately high temperatures, and the oxides of gold are still less stable. The order of stability of these compounds affords another illustration of the decrease in electropositive character with increase in atomic weight.

Cuprous hydroxide is a substance seldom encountered and difficult to prepare. Its mode and extent of ionization are of interest. Direct measurements are impossible because the substance is too insoluble. In such a case, the degree of ionization would ordinarily be determined by studying the degree of

hydrolysis of cuprous salts. But here again a difficulty is encountered for, as will be explained below, soluble cuprous salts decompose spontaneously in aqueous solution into cupric salts and metallic copper. No reliable method is therefore available for determining the strength of cuprous hydroxide as a base, although the formation of simple cuprous salts by the action of acids leaves no question as to its basic properties. **Cupric hydroxide,** readily prepared by treatment of soluble cupric salts with a strong base, must be a moderately weak base, since salts like cupric sulfate are sufficiently hydrolyzed to give an acid reaction to their aqueous solutions. The hydroxide is readily converted into cupric oxide at about 100°, even when suspended in water.

Silver hydroxide is not known; every reaction which might be expected to give it leads, instead, to the precipitation of the oxide. Silver oxide dissolves to a slight extent in water, and it is supposed that the substance which is present in solution is the hydroxide. Measurements of the conductivity of the solution indicate that the hydroxide is a somewhat stronger base than ammonium hydroxide. This conclusion is verified by the fact that aqueous solutions of salts like the nitrate are practically neutral towards litmus, showing that hydrolysis is extremely slight. Aurous hydroxide is not known; auric hydroxide is very unstable, and possesses both feeble basic and acid properties.

Although exact comparisons are impossible because of lack of data for all of the corresponding compounds, it is evident that the hydroxides become less strongly basic and less stable with increase in atomic weight, in accordance with the decrease in "positiveness" of the elements. The fact that cuprous and aurous hydroxides are stronger bases than the corresponding cupric and auric compounds, agrees with an observation, repeatedly made in other groups—namely, that the hydroxides of an element in which the latter exhibits its higher positive valence numbers are weaker bases than the hydroxides in which the valence number is low.

Complex Ions.—When ammonia is added to a suspension of cupric hydroxide in water, the solid disappears. The resulting

solution has an intense, dark blue color quite different from the lighter blue of solutions containing ordinary cupric ion. The marked color change is an indication that a new compound, probably containing a new ion, has been formed. Before attempting to decide on the nature of this compound, it is necessary to determine which of the various substances present in the original suspension are involved in the reaction. Copper ion must be one of the reactants for all soluble copper salts give compounds of the same blue color when treated with ammonia. But a solution of the latter is a fairly complex mixture; it contains free ammonia, ammonium hydroxide, ammonium ion and hydroxide ion. It is easy to prove that neither ammonium nor hydroxide ions are responsible for the reaction, for if they were, any solution containing them should behave toward copper hydroxide just as does aqueous ammonia. Ammonium salts are more highly ionized than ammonium hydroxide, yet neither ammonium chloride nor sulfate nor nitrate produces the deep blue compounds. Strong bases, such as sodium or potassium hydroxide, have no effect on copper salts, other than to precipitate the hydroxide.[1] Therefore neither ammonium nor hydroxide ions are of importance in the reaction in question. Ammonium hydroxide is excluded by the fact that dry copper salts absorb ammonia to form deep blue substances which, when dissolved, in water, behave just like the blue solutions. The reaction in question must therefore take place between cupric ion and ammonia. It has been shown to be:

$$Cu^{++} + 4NH_3 \rightleftarrows Cu(NH_3)_4{}^{++} \qquad (3)$$

It is now quite easy to understand why cupric hydroxide dissolves when ammonia is added. In the suspension of the hydroxide in water an equilibrium is established:

$$\underset{\text{solid}}{Cu(OH)_2} \rightleftarrows Cu^{++} + 2OH^- \ ^{2} \qquad (4)$$

[1] Cupric hydroxide, apparently because of slight acid properties, is soluble in very concentrated solutions of strong bases. The concentration of hydroxide ion required to dissolve copper hydroxide in this way is enormously greater than that present in the ammonia solutions under discussion.

[2] Equilibria of this type have been discussed in Chapter XV, page 238.

The reaction is displaced toward the right by the removal of copper ions to form the **copper ammonium ion**[3] when ammonia is added.

The formation of the copper ammonium ion is a reversible process, as indicated by the use of the double arrow in equation (3). This may be shown in a variety of ways. According to Le Chatelier's rule the removal of either ammonia or of cupric ion from the solution should drive the reaction to the left, or, in other words, should decompose the complex ion. Ammonia is readily driven from an aqueous solution by boiling; heating the solution obtained by dissolving copper hydroxide in ammonia causes reprecipitation of copper hydroxide. Evidently the ammonia is removed, the complex ion is decomposed, and the simple copper ions and hydroxide ions, left in the solution, unite to form copper hydroxide. Ammonia may be removed also by causing it to unite with hydrogen ion. Hydrochloric or any other strong acid discharges the intense blue color of the complex ions and brings back the color of ordinary copper ion. On the other hand, removal of copper ion may also be effected by the precipitation of a very insoluble copper salt, such as copper sulfide, from the deep blue solution.

The various reactions in which the cupric ammonium ion is decomposed illustrate its relative degree of stability. Ammonia dissolves a suspension of copper hydroxide; hence, the concentration of copper ions in a solution of the complex is smaller than in a saturated solution of cupric hydroxide. On the other hand, the decomposition of the complex ion by a sulfide indicates that the equilibrium represented in equation (3) is attained before the cupric ions are completely converted into complex ions, and that the concentration of cupric ions present at equilibrium is greater than their concentration in a saturated solution of copper sulfide. Evidently, copper sulfide must be considerably less soluble than copper hydroxide. Finally, the decomposition of the complex ion by acids shows that ammonium ion is less dissociated into ammonia than is the cupric ammonium ion.

[3] A number of different names have been proposed for this and other ions of similar character. The name which is most logical and most favored at present for the ion, $Cu(NH_3)_4^{++}$, is **tetrammine cupric ion.** The simpler name is nevertheless used in this text because it is unnecessary at present to burden the student with new terminology, and because it is desired to emphasize the similarity between these complex ions and ammonium ion.

The ability to unite in the formation of complex ions is limited neither to cupric ion nor to ammonia. Cupric ion reacts with many un-ionized substances and with other ions as well, to form complex ions, and the same is true of many other metal ions. In general, the formation of fairly stable complex ions is a **characteristic of the metals of the inner series of the periodic system,** although the division of outer and inner group metals on this basis is not an absolutely sharp one.[1] A number of additional illustrations, chosen for the present from the copper group elements, are of interest.

There are many reasons for believing that what has thus far been called simply the cupric ion is in itself a complex ion of relatively low stability. Anhydrous cupric sulfate is a white substance which becomes blue when it takes up water. Very likely the reaction is:

$$Cu^{++} + 4H_2O \rightleftarrows Cu(H_2O)_4^{++} \quad ^{2,3} \qquad (5)$$

Many other metal ions form complex ions with water. Those of trivalent chromium are particularly stable, and many of the

[1] Ions such as sulfate, phosphate, nitrate, etc., have been called compound ions rather than complex ions in this text. It is by no means certain that a sharp distinction should be drawn between the two types. Until the structural relationships of both classes are understood the question cannot be answered. It seems likely, however, that in the compound ions the atoms are held together by shared electron pairs, and that the number of atoms involved is determined by the requirement of completing octets; in the complex ions residual electromagnetic fields may possibly draw the molecules together, and the numerical relationships may be determined by geometric properties of space, rather than by the properties of the individual atoms involved. Werner's theory of complex ions is based on the geometrical concept. See Chapter XXXIX, page 572.

[2] The formula of completely hydrated copper sulfate is $CuSO_4 \cdot 5H_2O$. Probably the fifth water molecule is attached to the sulfate ion. The fact that sulfuric acid forms the very stable hydrate, $H_2SO_4 \cdot H_2O$, supports this view but further evidence is required before a decision can be reached.

[3] On the basis of this idea the formation of cupric ammonium ion is a replacement of water by ammonia in the complex ion:

$$Cu(H_2O)_4^{++} + 4NH_3 \rightleftarrows Cu(NH_3)_4^{++} + 4H_2O$$

This means that the complex with ammonia is more stable than that with water.

puzzling color changes of chromium salts are due to changes in the number of water molecules in the complex ion. There is no doubt that in many hydrates the water is attached to one of the ions (usually the positive ion) to form complex ions like that postulated for cupric salts. The explanation of hydrate formation will probably be simple once the structure of complex ions is fully understood.

Another interesting illustration is the series of changes which occur when cupric bromide is dissolved in water and the solution is diluted. Solid cupric bromide is almost black. Its saturated aqueous solution is very dark and of a deep reddish-brown cast. The color gradually changes with successive additions of water, becoming first yellower, then greenish, and finally turning to the characteristic blue of dilute copper solutions. It was at one time thought that un-ionized cupric bromide is the dark substance which imparts its color to the concentrated solutions, and that the color changes are due to the increase in degree of ionization with increasing dilution. It has since been shown that this interpretation is not correct. Obviously it is not in keeping with our present views of the nature of salts. According to recent theories and X-ray analyses of simple salt crystals, salt molecules are aggregates of positive and negative ions held together in definite proportions by electrostatic attraction. Whether the degree of freedom from these attractions changes as solutions are diluted has not yet been settled, but there is nothing in the modern viewpoint to account for a difference in color between ions and molecules of a salt.

Another interpretation of the behavior of cupric bromide has been developed from a large amount of research. One of the most significant facts brought out by this work is that electrolysis of a concentrated aqueous solution of the salt draws some of the copper to the positive pole, and some to the negative pole. Evidently copper is present both in the negative and in the positive ion. Cupric bromide must therefore have the formula Cu_2Br_4 rather than $CuBr_2$, and ionize, in concentrated solution, according to the equation:

$$Cu_2Br_4 \rightleftarrows Cu^{++} + CuBr_4^{=} \qquad (6)$$

As dilution proceeds, water molecules replace bromide ions in the complex ions:

$$CuBr_4^{=} + 4H_2O \rightleftarrows Cu(H_2O)_4^{++} + 4Br^{-} \qquad (7)$$

At the same time the anhydrous copper ions [1] also unite with water. When enough water has been added, the solution contains nothing but the bromide ion and hydrated cupric ions. It therefore shows only the color of the latter, since bromide ion is colorless. The color changes just discussed may be reversed by adding an excess of potassium bromide to the diluted cupric bromide solution. By thus increasing the concentration of bromide ion the reaction (equation (7), is reversed, and the dark brown $CuBr_4^{=}$ ion is again formed.[2] Attention is called to the fact that cupric tetrabromide ion is negative, because the four negative charges of the bromine ion counterbalance the two positive charges on cupric ion; the complex ion becomes two positive when bromide ion is replaced by water molecules, which possess no charges.

Silver ions likewise form a large number of complex ions. Silver oxide, which has no acid properties, dissolves readily in aqueous solutions of ammonia on account of the formation of the complex ion, $Ag(NH_3)_2^{+}$.[3] When sodium chloride is added to a solution containing exactly 2 gram molecules of ammonia for one of silver oxide, silver chloride is precipitated; but the addition

[1] The phenomena have been described in their simplest aspect. Hydration of cupric ion unquestionably takes place immediately when cupric bromide is dissolved and is the first step in the changes which occur. The change from the complex cupric tetrabromide ion to the tetra-aquo cupric ion occurs in steps; the bromide ions are replaced one at a time by water, so that complex ions of the type $(CuBr_3 \cdot H_2O)^{-}$ and $(CuBr \cdot 3H_2O)^{+}$ are probably formed.

[2] Addition of enough potassium bromide might conceivably convert all of the cupric ion into the bromide complex. In this case there would be no cupric ions to pair with the negative ions, but there would be just enough potassium ions left to do so, as shown by the equation:

$$Cu(H_2O)_4Br_2 + 2KBr \rightleftarrows K_2(CuBr_4) + 4H_2O$$

[3] Solutions of silver salts in ammonia must not be allowed to evaporate to dryness, or even to become highly concentrated, because of the danger of violent explosions.

of an excess of ammonia redissolves the precipitate. Evidently the formation of the silver ammonium ion is also a reversible process:

$$Ag^+ + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ \qquad (8)$$

Without an excess of ammonia enough free silver ions are left in the solution at equilibrium to precipitate the chloride; excess of ammonia drives reaction (8) sufficiently far to the right to prevent precipitation. But silver ions are not completely removed even by the greatest possible amount of ammonia, because even under these conditions very insoluble silver sulfide is precipitated from the solution.

Even silver sulfide is dissolved by the addition of potassium cyanide. The latter reacts with silver ion to form the complex silver cyanide ion, $Ag(CN)_2^-$, which evidently furnishes so few silver ions that even silver sulfide cannot be precipitated from its solutions. The equation for the reaction in which silver sulfide is dissolved is:

$$Ag_2S + 4KCN \rightleftarrows 2K(Ag(CN)_2) + K_2S \qquad (9)$$

The complex ion formed by the union of silver and thiosulfate ions, $Ag(S_2O_3)_2^{=}$, is of importance in photography. (See page 517.) Gold is also found as a constituent of a large number of complex ions. The formation of the $AuCl_4^-$ ion in the action of aqua regia on metallic gold has already been discussed (page 321); gold dissolves also in potassium cyanide because of the formation of a complex ion, $Au(CN)_2^-$.

Salts with Complex Ions and Double Salts.—When a mixture of copper and ammonium sulfates is evaporated, there are deposited large crystals of a salt the formula of which is usually written $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. When the salt is redissolved, it yields a solution which possesses all of the properties of a mixture of cupric and ammonium sulfates, and no properties which cannot be accounted for by the presence of these two substances. In this respect it differs from salts with complex ions, such as $Cu(NH_3)_4SO_4$ formed by addition of ammonia to cupric sulfate. This complex salt possesses the deep blue color characteristic of the $Cu(NH_3)_4^{++}$ ion rather than the color of cupric ion, it does not react with sodium

hydroxide to precipitate cupric hydroxide, and does not behave in other ways like a mixture of cupric sulfate and ammonia. Substances like $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ are known as **double salts.** Evidence for their existence is found only in the solid state. It is quite probable that they, like hydrates, are similar to complex salts, but that the complex ions which they contain are so unstable that they are largely decomposed in solution. On the other hand it is also possible that, in some instances at least, double salt formation is closely related to crystal formation; that is, that association of the two components occurs in the process of building up a close-packed arrangement of the ions or molecules when the material solidifies. The problem is still unsolved.

Cuprous Salts.—Cuprous salts are usually prepared by the reduction of cupric salts. The reaction involved is:

$$Cu^{++} + \epsilon \rightleftharpoons Cu^{+} \qquad (10)$$

As shown by the relative lengths of the two arrows, cupric ion has a relatively small tendency to take up 1 electron and go over to cuprous ion; a fairly strong reducing agent is therefore required to effect reduction. On the other hand cuprous ion has a very strong tendency to be reduced to copper. Reduction to copper may be brought about by the action of a reducing agent according to the equation:

$$Cu^{+} + \epsilon \rightleftharpoons Cu \qquad (10a)$$

It may also be the result of spontaneous decomposition of a cuprous salt into a cupric salt:

$$2Cu^{+} \rightleftharpoons Cu^{++} + Cu \qquad (10b)$$

Since reaction (10*a*) has a greater tendency to go to the right than has reaction (10), any reducing agent strong enough to reduce cupric to cuprous compounds, must also be strong enough to reduce the latter to free copper. Likewise, since reaction (10*b*) also has a very great tendency to go to the right, cuprous salts, if formed in aqueous solution, must decompose into cupric salts and copper. Cuprous salts can therefore be produced only under conditions such that the cuprous ion is removed from solution as soon as it is formed.

This may be accomplished either by causing the cuprous ions to precipitate as insoluble salts, or to form a complex ion with some other substance present. The formation of cuprous salts by precipitation of an insoluble compound is illustrated by the action of potassium iodide on copper sulfate:

$$2CuSO_4 + 4KI \rightarrow 2CuI\downarrow + I_2 + 2K_2SO_4 \qquad (11)$$

The influence of complex ion formation in the preparation of cuprous salts is illustrated by the action of copper on cupric chloride [1] in the presence of hydrochloric acid. The reaction is essentially reaction (10*b*) proceeding to the left. In the absence of an excess of chloride ions, there is no interaction between cupric chloride and copper because under these conditions reaction (10*b*) goes almost completely to the right. But the addition of concentrated hydrochloric acid furnishes a large excess of chloride ions which unite with cuprous ions to form a complex ion:

$$Cu^+ + 2Cl^- \rightleftarrows CuCl_2^{-} \text{ [2]} \qquad (12)$$

The removal of the cuprous ions in this way causes reversal of the ordinary course of reaction (10*b*). The equation for all of the changes occurring in the action of copper on cupric chloride in the presence of hydrochloric acid is:

$$CuCl_2 + Cu + 2HCl \rightleftharpoons 2HCuCl_2 \qquad (13)$$

The substance $HCuCl_2$ is known only in solution. In contrast to solutions of cupric salts, it is colorless. When the solution is diluted the compound decomposes into white, very slightly soluble cuprous chloride and hydrochloric acid:

$$HCuCl_2 \rightleftarrows CuCl + HCl \qquad (14)$$

Reaction (14) is reversible; cuprous chloride may be redissolved in an excess of concentrated hydrochloric acid and then reprecipitated by the addition of water. By carrying out these reactions

[1] Any other salt furnishing cupric ion might of course be used.

[2] Several complex ions of cuprous and chloride ions seem to exist. If the excess of hydrochloric acid is large, the ion $CuCl_3^{=}$ is formed in addition to the one mentioned.

once or twice, cuprous chloride may be purified from any traces of cupric salt adhering to it.[1]

Further comparison of the methods of preparation of cuprous iodide and cuprous chloride, brings out one other point of interest. Reaction (11) may be divided into two steps:

$$2CuSO_4 + 4KI \rightleftarrows 2CuI_2 + 2K_2SO_4 \qquad (11a)$$

and

$$2CuI_2 \rightarrow 2CuI + I_2 \qquad (11b)$$

In other words, cupric iodide, formed by double decomposition of soluble cupric salts and soluble iodides, decomposes spontaneously into cuprous iodide and iodine. Cupric chloride does not undergo an analogous decomposition. In reaction (11*b*) iodide ions perform two functions. They give up electrons to reduce cupric to cuprous ions, and then the iodide ions left unite with the cuprous ions to form insoluble cuprous iodide. Chloride ion is capable of performing the second function, that is of removing cuprous ions by forming an insoluble salt or a complex ion, but it does not give up electrons readily enough to reduce cupric salts.

From the considerations of the preceding paragraph it is evident that the most stable cuprous salts must be those which not only are insoluble, but also contain a negative ion capable of acting as a strong reducing agent. In agreement with this conclusion, the most readily prepared cuprous salts are the iodide, the cyanide, the sulfide and the bromide. The first two are formed by spontaneous decomposition of the corresponding cupric salts, while the last two may be obtained by heating the cupric salts. These differences are in agreement with the fact that iodide and cyanide ions are better reducing agents than sulfide or bromide ions.[2]

[1] The formula for cuprous chloride is often written Cu_2Cl_2. The vapor of the substance near the boiling point has a density corresponding to the double formula, and the molecular weight of concentrated solutions of the salt in various non-aqueous solvents also indicates the same formula. In dilute solutions, however, the formula appears to be CuCl. The double formula may represent a cuprous salt of the acid $HCuCl_2$, i.e., $Cu(CuCl_2)$.

[2] Cupric cyanide decomposes into the cuprous salt according to the equation: $2Cu(CN)_2 \rightarrow 2Cu(CN) + (CN)_2$. The last substance is the very poisonous gas, cyanogen. It is therefore dangerous to add a cyanide to a solution containing copper salts, except in alkaline solution in which the cyanogen is oxidized to cyanates.

Cuprous Salts.—Most of the important properties of cuprous salts have been brought out in the preceding discussion. They are usually white or very pale yellow, but are readily discolored by partial hydrolysis to the very insoluble, red cuprous oxide, and by oxidation to cupric salts. They are extremely readily oxidized by air and other oxidizing agents, and decompose in solution spontaneously into cupric salts and copper unless the cuprous ion is present as part of a stable complex ion. They form a great number of such complexes. Cuprous salts react with carbon monoxide to form a compound which is in some ways analogous to the compound of ferrous salts with nitric oxide. (See page 311.) Use is made of this fact in absorbing carbon monoxide for analysis.

Cupric Salts.—With the exception of the chloride, bromide, nitrate and sulfate and a few salts of organic acids, most of the cupric salts are very slightly soluble in water. Since cupric hydroxide is not a strong base, the salts are somewhat hydrolyzed. Their ability to form double salts and complex salts has already been mentioned; the formation and solubility relations of cupric sulfide were discussed on page 252. Since copper is much less electropositive than the alkali and alkaline earth group metals, its carbonate, nitrate, and sulfate are much more readily decomposed into the oxide by heat than are the corresponding salts of these metals.

The uses of most copper salts need no further discussion, but two of them will be mentioned to correct a very common error. The names verdigris and Paris green are often applied indiscriminately to green compounds of copper. **Verdigris** is a basic acetate of copper ($Cu_3(OH)_2(C_2H_3O_2)_4$) which is obtained by the action of acetic acid (vinegar) on copper in the presence of air. It is used in paint manufacture. **Paris green,** used chiefly as an insecticide, is a double salt of copper acetate and copper arsenite ($3Cu(AsO_2)_2 \cdot Cu(C_2H_3O_2)_2$). **Fehling's solution** has been mentioned so often in this text that its method of preparation is of interest even though an understanding of its chemical character is impossible without some knowledge of organic chemistry. It is obtained by dissolving cupric hydroxide in an alkaline solution of sodium potassium tartrate, $NaKC_4H_4O_6$; copper replaces hydrogen in hydroxyl groups of the tartrate, and is found in the negative ion of the resulting compound. It is used to oxidize sugars and other organic compounds because they are acted on more readily in alkaline than in neutral or acid

solutions; in the absence of substances like tartrates, copper salts are precipitated and thus rendered inactive by alkalies.

Silver Salts.—Silver salts, as is to be expected, resemble cuprous rather than cupric salts in their solubility relations. The halides, except silver fluoride, are insoluble in water, as are most of the other silver salts except the nitrate, sulfate and chlorate. As has already been pointed out, silver salts are less hydrolyzed than cupric salts and probably less hydrolyzed than cuprous salts, although for the latter no exact measurements are available. Since silver is 1+ in all of its compounds, its salts are not reducing agents; but as silver ion has considerable tendency to revert to the metallic condition by gaining 1 electron, the salts of silver are moderately strong oxidizing agents. This is shown in their action with formaldehyde, which reduces silver salts to free silver. The reaction is used in silvering mirrors.[1] Silver nitrate, carbonate, sulfate and other similar salts are more readily decomposed by heat than the corresponding copper salts. This fact agrees with the greater " positiveness " of copper. At temperatures high enough to decompose the oxide, metallic silver is of course obtained.

Action of Light on Silver Salts.—Many silver salts are decomposed by the action of light. The effect is particularly noticeable in the case of the chloride and bromide. Freshly precipitated silver chloride is pure white; on exposure to bright light, it rapidly acquires a greyish-blue color. Just what the chemical character of the change is, has not yet been definitely decided. Silver salts which have been affected by light are much more rapidly reduced by various reagents than are the unexposed salts. This fact is the basis for present photographic methods.

A sensitive plate or film is made by coating glass or cellulose acetate with a suspension of very finely divided silver halide in gelatine. (The coating is inaccurately called an emulsion.) The preparation of the halides as well as the manufacture of plates or films must of course be carried out in the dark. When an image of

[1] For the reasons mentioned in connection with Fehling's solution, it is necessary to use the silver salts in alkaline solution. To prevent precipitation of silver oxide, ammonia is added. Silvering solutions containing ammonia must not be kept long. (See footnote 3, p. 510.)

some object is projected upon such a plate or film in a camera, those parts of the suspension which receive intense illumination become very readily reducible while those upon which the illumination is less intense are less reactive. Consequently, after the exposed plate or film has been placed in a bath containing a reducing agent, the bright features of the object are represented by dark areas on the plate or film, due to the deposition of a relatively large amount of metallic silver by the reducing agent. The darker features of the object are represented by lighter deposits of silver, while the features from which no light was reflected produce no deposits. The object is therefore seen on the plate or film as a " negative." Should the negative now be exposed to illumination the portions not reduced by the bath would gradually darken because of the action of light. The negative must therefore be " fixed."

The fixing of the negative is accomplished by treating it with a reagent which dissolves the light sensitive silver salts, but does not affect the metallic silver. Sodium thiosulfate (incorrectly called hyposulfite or " hypo ") is frequently used. It is effective because the thiosulfate ion unites with the silver ion to form a very stable complex ion. Silver chloride or bromide is thus dissolved because of the removal of silver ion. The process of making a positive is entirely analogous to that of making the negative, except that, instead of affecting the light sensitive paper by illumination from the object to be photographed, light falling through the negative is used. " Toning " of prints is effected by treating them with solutions containing gold or platinum ions. These are displaced from solution by silver, and the deposited gold or platinum imparts special colors and character to the picture. Silver bromide is used in place of silver chloride in the " emulsions " for particularly fast, that is sensitive photographic papers.

Compounds of Gold.—Gold is so slightly electropositive that it forms very few salts in which it takes the part of a simple positive ion. Those which do exist are easily decomposed. Even gold fluoride and chloride are decomposed into the free elements at moderately high temperatures; the existence of salts of oxygen acids such as sulfates or nitrates has not been demonstrated with certainty. Aurous salts are somewhat similar to cuprous salts. Thus aurous chloride is but slightly soluble in water. In dissolv-

ing, aurous salts decompose into auric salts and free gold just as cuprous salts on dissolving decompose into cupric salts and copper. On the other hand auric iodide decomposes slowly into insoluble aurous iodide, but the reaction is not so rapid nor so nearly complete as the corresponding reaction of cupric iodide.

Gold shows a very pronounced tendency to form complex compounds. The rôle which the complex ions of gold with chloride and with cyanide ions play in processes for dissolving the metal has already been mentioned. The same tendency is responsible for the fact that gold sulfides, unlike silver or copper sulfides, are soluble in sodium or ammonium sulfide. This reaction is brought about by the formation of complex ions of gold and sulfur. Concerning the composition of these ions there is still some uncertainty. It will be recalled that arsenic and antimony sulfides also dissolve in ammonium or sodium sulfide on account of the formation of complex ions.[1]

Hydrides of the Group.—Compounds supposed to be hydrides have at various times been described, but the most reliable evidence at the present time is that no compounds of this type are formed by the elements of the group. The red material frequently called copper hydride has been shown to consist of finely divided copper which has absorbed or dissolved large amounts of hydrogen. In this respect the elements of the group differ markedly from the outer group elements thus far discussed.

Alloys.—Attention is called to the numerous important alloys of the metals of the group with each other and with metals of other groups. The influence of the various bronzes and other copper alloys in the development of civilization is a part of history, and it may be assumed that the reader is familiar with it; in the same way the uses of gold and silver have been so often described in connection with the history of human progress, that repetition in this text is out of place.

[1] The fact that gold hydroxide has acid properties may be interpreted as being due to formation of complex ions with oxygen ion. If it is assumed that the ionization of auric hydroxide as a base leads to the formation of Au^{+++} and $3OH^-$, the behavior of the same substance as an acid may mean that the gold ions react with hydroxide ions to give a complex gold-oxygen ion and hydrogen ion, as represented in the equation:

$$Au^{+++} + 2OH^- \rightleftarrows AuO_2^- + 2H^+$$

EXERCISES

(1) Suggest a method for precipitating silver from the aqueous solution obtained from silver sulfide ores by the process mentioned on page 499.

(2) Judging from the reaction represented by equation (2), page 499, which should you consider to be more electropositive, silver or mercury?

(3) In Parke's process for separating silver from lead, why does silver rise to the top with zinc instead of remaining in the lead?

(4) Explain in detail how copper is separated from the more active and from the more inactive metals in the electrolytic process of purification.

(5) Cite all of the facts which you can, to corroborate the statement that copper is more positive than silver, and silver more positive than gold. (The answer to this question should deal not only with the properties of the free metals, but also with those of their compounds, as for example, strength and stability of the bases, oxidizing power and stability of the salts, etc.)

(6) Describe the phenomenon of passivity.

(7) What are the methods for determining the strength of an hydroxide as a base? Why are these methods not applicable to cuprous hydroxide?

(8) What is the evidence that the blue color obtained by addition of ammonia to cupric salts is due to a complex ion of ammonia and cupric ion?

(9) Explain why cupric hydroxide dissolves in aqueous ammonia. In your explanation what assumption is made about the relative concentration of cupric ions in a saturated solution of cupric hydroxide and in a solution of the cupric ammonium ion?

(10) Write the equation for the reaction which occurs when cupric sulfide is precipitated from a solution of cupric ammonium hydroxide by the addition of ammonium sulfide.

(11) In view of the explanation given for the color changes occurring when cupric bromide is diluted, predict what color changes should occur near each of the 2 electrodes when a fairly concentrated solution of cupric bromide is electrolyzed.

(12) Why is an excess of ammonia required to dissolve silver chloride?

(13) What is the difference in behavior between double and complex salts?

(14) Which is the stronger oxidizing agent, cupric or cuprous ion? (Before answering, consider carefully the statements on page 512 concerning the action of reducing agents on cupric salts.)

(15) Cuprous ion normally tends to decompose into cupric ion and copper. Why do copper and cupric ion react to form cuprous ion in the presence of hydrochloric acid?

(16) Why does cupric iodide decompose spontaneously whereas cupric chloride is stable in solution?

(17) Make a table of the differences between the alkali metal and the copper groups. The table should include comparisons based on at least the following points: (*a*) physical properties of the metals, (*b*) valence relations in the two groups, (*c*) electropositive character of the groups as a whole, (*d*) relationship of atomic weight to positive character in the two groups, (*e*) reducing power of the metals of the two groups as illustrated in their action with air, with water and with nitric acid, (*f*) strength of the hydroxides as bases, including the way in which this property changes with increase in atomic weight, (*g*) oxidizing power and stability of the salts, (*i*) tendency toward complex ion formation.

(Note.—Some of the points suggested may be outlined for the group as a whole, in others the behavior of the individual metals of one or the other group may have to be treated separately. Other points may be added to make the outline more complete.)

REFERENCES

H. Wysor—Metallurgy (1914). Chapters XVIII, XIX, XX, XXVI and XXVII for details about the metallurgy of the elements of the group.

See also the general references cited in Chapter XXXII and the special reference on complex ions in Chapter XXXIX of this text.

CHAPTER XXXV

THE ZINC GROUP

Although the individual elements of the zinc group, zinc, cadmium and mercury, differ decidedly from the elements of the copper group, the group characteristics are not unlike. In both groups the valence is not the same throughout; zinc is two positive in all of its compounds, while cadmium and mercury are one positive in cadmous and in mercurous compounds and two positive in the ordinary cadmium and in mercuric compounds. Cadmous compounds are, however, very rare. As in the copper group, the valence common to the three elements is the characteristic group valence. In both groups electropositiveness decreases with increasing atomic weight, in contrast to the increase in positiveness observed in outer groups. With the exception of the halides, sulfates, nitrates and a few others, most of the salts are but slightly soluble; the mercurous halides, like those of univalent copper and of silver, do not dissolve appreciably in water. The elements of both groups are capable of forming numerous complex ions, the salts of which are much more soluble than the salts of the simple ions. The zinc group is, as a whole, far more electropositive than the copper group, but less positive than the alkaline earth group which corresponds in the outer series to the zinc group in the inner series.

Occurrence and Manufacture of the Elements.—Zinc is found chiefly as the sulfide (zinc blende) and carbonate (smithsonite); cadmium in the analogous compounds, frequently associated in small amounts with zinc ores; mercury as the red sulfide, cinnabar, and as the free metal. Zinc and cadmium ores are converted into oxides by heat or by roasting in a stream of air, and are then reduced to the metallic condition by carbon. Cadmium boils at 770°, zinc at 929°; these temperatures are so low that the elements

are volatilized by the heat of the reduction furnaces, and are collected by condensing the vapors. Cadmium, which has the lower boiling point, distills over first, and separation of the two metals may thus be effected. When mercuric sulfide is heated in air, it is also presumably first converted into the oxide, but this decomposes at once into the free metal. Mercury volatilizes in the process since it has a boiling point of only 357°.

Properties of the Metals and their Uses.—The elements are typical metals of relatively low boiling and melting points.[1] Zinc is somewhat brittle at ordinary temperatures. At 100–150° it becomes ductile enough to be rolled or drawn, but at 200° it is again so brittle that it can be powdered. Zinc vapor burns in air, but the compact metal does not rust extensively at ordinary temperatures because it becomes coated with a fairly impervious, closely adhering layer of a basic carbonate. For this reason it is used for making gutters and cornices on buildings. Iron is coated with zinc by dipping thoroughly cleaned iron sheets or wire into molten zinc (galvanizing), by electroplating, or by covering the iron with zinc dust and baking it (sherardizing). The zinc protects the iron from the action of air, but even when the coating of zinc is broken, protection is afforded to the iron object because the zinc is attacked in preference to the iron when the two are in contact, as will be explained in Chapter XXXVIII. Zinc is extensively used in alloys such as babbitt, brass and German silver. Powdered zinc (zinc dust) is a widely used reducing agent.

Cadmium is acted on by air even less readily than zinc; its use is, however, limited to the making of fusible alloys since it is not very abundant. Mercury reacts so slowly with oxygen at ordinary temperatures that the action is inappreciable; at 100° the reaction is still very slow. At higher temperatures the oxide is decomposed again into the free metal. The uses of mercury depend largely on the fact that it is liquid at ordinary temperatures, and very dense. Its employment in barometers and thermometers is a matter of common knowledge.

The differences in the effect of oxygen on the three metals is evidence of the fact, already stated, that zinc is the most and mercury the least electropositive of the group. Indicative of the same

[1] The exact data are given in Table XXII, page 463.

difference are the facts that zinc liberates hydrogen from steam at high temperatures and from cold aqueous solutions of acids; furthermore it reduces nitric acid to ammonium nitrate. Mercury does not act on water or acids to liberate hydrogen, and reduces nitric acid only to nitrogen tetroxide. Cadmium lies between zinc and mercury in these respects. Zinc is, in other words, a moderately good reducing agent, mercury a poor one. Conversely, zinc ions take up electrons with so little readiness that zinc salts do not act as oxidizing agents, while mercury salts are moderately good oxidizing agents.

It is of interest to compare the behavior of the elements of the zinc group in these respects with the alkaline earth metals on the one hand, and with those of the copper group on the other. The alkaline earth group metals are all more powerful reducing agents than any of the zinc group metals, as is shown by the action of the former toward air, water, acids and oxidizing agents, and by the fact that they displace the elements of the zinc group from solution under suitable conditions. The elements of the copper group, on the other hand, are much less readily attacked by air than either zinc or cadmium, they do not act at all with water or with acids to displace hydrogen, and do not reduce nitric acid as completely as do zinc or cadmium. Mercury, however, is less positive than silver or copper, but it is more positive than gold.

The Oxides and Hydroxides.—The **oxides** of zinc and cadmium are stable toward heat, those of mercury unstable. The gradual transitions in color are of interest; zinc oxide is white at ordinary temperatures, but yellow when hot; cadmium oxide is brown; mercurous oxide is black, and mercuric oxide yellow or red, depending on the method of preparation and the size of the particles. None of the oxides is soluble in water. The **hydroxides** of zinc and of cadmium are white, insoluble substances, readily prepared by the action of solutions of strong bases on the corresponding salts, and easily decomposed by heat into the oxides; the hydroxides of mercury are not known to exist, for reactions which might lead to their formation cause immediate precipitation of the oxides. Zinc hydroxide is a moderately weak base as is shown by the fact that its salts with strong acids are decidedly acid in solution; both mercurous and mercuric oxides act as the

anhydrides of very weak bases since mercurous and mercuric salts are extensively hydrolyzed in water.[1]

Zinc hydroxide, although not a very weak base, is capable of acting also as an acid. In other words, the molecules of zinc hydroxide are capable of ionizing in two ways as shown by the two equations:

$$Zn(OH)_2 \rightleftarrows Zn^{++} + 2OH^-$$

and

$$Zn(OH)_2 \rightleftarrows ZnO_2^{=} + 2H^+$$

The addition of a strong base to zinc hydroxide drives the former reaction to the left because of the addition of an excess of hydroxide ions; at the same time it drives the second reaction to the right because the added hydroxide ions react with hydrogen ions to from water. Similarly, addition of a strong acid drives the second reaction to the left, and the former to the right. In other words, when a base is added, zinc hydroxide acts like an acid; when an acid is added, zinc hydroxide acts like a base. This behavior is illustrated by the facts that zinc hydroxide is soluble either in an acid or in a base. With acids it forms the simple zinc salts; by interaction with bases it forms the zincates, such as Na_2ZnO_2. It is interesting to note that zinc hydroxide is the only one of the group which is amphoteric.

Although zinc hydroxide is both a base and an acid there is no evidence that it " neutralizes itself." Zinc hydroxide is a moderately weak base and a very weak acid; a salt of the two would be practically completely hydrolyzed in aqueous solution; it could therefore not be formed, since only in solution does zinc hydroxide display its acid and basic characters.

[1] No statement is made concerning the strength of cadmium hydroxide as a base because information on this point seems very incomplete. Cadmium chloride is but slightly hydrolyzed in aqueous solutions. This fact might be taken to indicate that the hydroxide is at least a moderately strong base. But cadmium chloride does not exist in aqueous solutions entirely as the simple salt, $CdCl_2$; an unknown, but fairly large percentage of the substance is present as the complex salt $Cd(CdCl_4)$. Since nothing is known of the strength of the hypothetical acid, H_2CdCl_4, conclusions about the degree of hydrolysis of the complex salt cannot be safely drawn from the action of its salts on indicators.

Complex Ions.—All of the elements of the group form complex ions. Zinc hydroxide, for example, is soluble in aqueous ammonia. The reaction is not due to the formation of ammonium zincate. Zinc hydroxide is a very weak acid and ammonium hydroxide a weak base; hence a salt of the two would be nearly completely hydrolyzed by water. Furthermore, 2 gram molecules of ammonium hydroxide would be required to neutralize 1 of zinc hydroxide, acting as an acid, but to dissolve zinc hydroxide, 4 gram molecules of ammonia are actually used. It has been shown that the formation of the complex ion, $Zn(NH_3)_4^{++}$, is responsible for the solubility of zinc compounds in ammonia. Cadmium forms an entirely analogous ion with ammonia, and both metal ions unite with cyanide ions to form complex ions of the type, $Cd(CN)_4^{=}$. In concentrated solution, cadmium chloride exists largely as the salt, $Cd(CdCl_4)$[1]; similar complex salts are formed by the iodide and bromide. Mercuric iodide, which is very slightly soluble in water, dissolves in a solution of potassium iodide because the complex salt, $K_2(HgI_4)$, is formed.[2]

Ammono Compounds of Mercury.—Mercury ions do not form stable complex ions with ammonia, but interact with the latter to give compounds analogous to basic salts. The first step in the hydrolysis of a salt like mercuric chloride may be represented by the equation:

$$HgCl_2 + HOH \rightleftarrows Hg(OH)Cl + HCl$$

This reaction is caused by the ionization of water into hydrogen and hydroxide ions, and by the small degree of ionization of mercuric hydroxide. Ammonia ionizes slightly into NH_2^- and H^+, and the reaction

$$HgCl_2 + HNH_2 \rightleftarrows Hg(NH_2)Cl + HCl$$

is analogous to the one written above. It is obvious, however, that the hydrochloric acid produced must react at once with additional

[1] The salt $Cd(CdI_3)_2$ is also known.

[2] It is possible that the color changes observed with mercuric iodide are due to complex formation. Addition of potassium iodide to a solution of a mercuric salt precipitates mercuric iodide $(HgI_2)_x$ as a yellow substance which at once turns red. On heating the dry substance, it changes again to yellow. When this is cooled, the yellow form may persist in a meta-stable condition. A slight scratch or jar on the vessel in which it is contained starts the rapid change into the red modification.

ammonia to give ammonium chloride. Because of the analogy between the basic chloride and the compound formed by ammonia, the latter is called **ammono-basic mercuric chloride.** This reaction is but one of many analogies in the behavior of water and of ammonia; a number of them have been pointed out on page 240. Other similar mercury salts are known. The highly colored compound, Hg_2NI, is formed when a solution of potassium mercuric iodide containing potassium hydroxide is treated with ammonia. The equation is:

$$2K_2HgI_4 + 4NH_3 \rightarrow Hg_2NI + 4KI + 3NH_4I$$

The reaction is the basis for the very sensitive **Nessler's** test for ammonia. Mercurous salts seem to react in similar fashion with ammonia, but the compounds formed are unstable and decompose into the corresponding mercuric compounds and free mercury. Mercurous chloride and ammonia yield an intensely black mixture of mercury and ammono-basic mercuric chloride.[1]

Mercurous and Mercuric Salts.—The fact that soluble mercurous salts, such as the nitrate, exist in aqueous solution shows that the tendency of mercurous ion to oxidize and reduce itself (thus forming free mercury and mercuric salts) is not so great as the corresponding tendency in cuprous salts. Mercurous salts may in general be formed by the reverse of this reaction, that is by the action of mercury on mercuric salts.

The direction in which the reaction,

$$2Hg^{+} \rightleftarrows Hg^{++} + Hg$$

proceeds is, of course, determined by the factors which always govern such equilibria. The removal of mercuric ion to form a very stable complex ion drives the reaction to the right; formation of insoluble mercurous salts favors action to the left. Mercurous iodide, for example, in the presence of an excess of potassium iodide, decomposes into free mercury and a mercuric salt; this happens because the mercuric ion is removed by iodide ion in the formation of the complex $HgI_4^{=}$. Other reducing agents besides free mercury itself may be used to prepare mercurous from mercuric

[1] Although mercury is not ordinarily black, the very dark color of the precipitate is usually accounted for by the assumption that the metallic mercury is colloidally dispersed. It is, however, very likely that the mixture also contains a small amount of mercurous oxide which is very deep black.

salt, but the difficulty is often encountered that in such reactions the mercurous salts are also reduced to free mercury. An illustration is found in the action of stannous chloride on mercuric salts; in the presence of an excess of the latter mercurous chloride is obtained:

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + 2HgCl$$

Addition of an excess of stannous chloride causes further reduction:

$$SnCl_2 + 2HgCl \rightarrow SnCl_4 + 2Hg$$

Even when an excess of stannous chloride is added at once, white mercurous chloride is first precipitated. It then gradually turns gray because of further reduction. The reaction is utilized in qualitative analysis.

Mercury salts are of interest because in many instances they are very slightly ionized.[1] Mercuric cyanide is practically a nonconductor of electricity; the halides though somewhat more ionized than the cyanide also are weak electrolytes. For these reasons they interact slowly with sulfuric acid to liberate the free halogen acids, and are not extensively hydrolyzed. Mercuric nitrate is ionized to the greatest extent. Possibly the low degree of ionization is related to the tendency toward complex formation, but this is at present merely a suggestion.

Salts of the Elements.—Little need be added concerning the compounds of the group. The chlorides are all moderately volatile substances which form hydrates and are so soluble that they readily deliquesce;[2] the salts of oxygen acids are less stable than the corresponding salts of the alkaline earth group. Zinc chloride is used in making cements and as a flux in soldering; zinc oxide as a pigment and in salves used for treatment of burns and wounds; other zinc salts medicinally, particularly as astringents. Mercury compounds are used in medicine and in surgery. Mercurous chloride (calomel), mercuric chloride (corrosive sublimate), mercuric oxide and mercuric iodide are most frequently employed. The exceedingly poisonous character of mercury and its com-

[1] Cadmium salts are, in this respect, similar to those of mercury, but the former are somewhat more extensively ionized than the latter.

[2] Except mercurous chloride, which is insoluble.

pounds is well known. It may be added that practically all mercury compounds are volatile; this fact must not be overlooked to avoid danger from poisoning in the laboratory. The indiscriminate use of zinc compounds in mouth washes, as well as in salves or dusting powders, is also not safe, for zinc is more poisonous than is generally known, and some individuals exhibit exceptional sensitiveness to its action.

EXERCISES

(1) Why is 2 positive considered the "characteristic group valence" of the zinc group?

(2) Which zinc ores can be converted to the oxide by heating alone, and which must be heated in a stream of air?

(3) Suggest how oxygen might be extracted from air by the use of mercury. Why is the method not practical?

(4) Arrange the elements of the group in the order in which they would displace one another from solution, putting the element which is displaced below the one which displaces it.

(5) Write the equation for the reduction of dilute nitric acid by zinc.

(6) Give all the evidence you can to show that zinc is more positive than copper and that mercury is more positive than gold.

(7) Suggest reactions by which one might attempt to prepare mercuric hydroxide. (The reactions all give the oxide instead of the hydroxide.)

(8) Explain in detail why zinc hydroxide ionizes more nearly completely as an acid when a base is added to it, and more nearly completely as a base when an acid is added.

(9) Explain by Le Chatelier's rule why zinc hydroxide dissolves in acid; why it dissolves in sodium hydroxide; why it dissolves in aqueous ammonia. Write equations for the reactions involved.

(10) Suggest a method for proving that cadmium chloride exists in solution as the complex salt, $Cd(CdCl_4)$.

(11) Complete the equation for the reaction of ammonia on mercuric chloride (page 525).

(12) Explain why mercurous chloride is nearly always formed in the action of stannous chloride on mercuric chloride, even though the reaction may ultimately proceed as far as the reduction of the mercurous chloride to free mercury.

(13) Suggest the probable order of the stability of the sulfates of the group.

REFERENCES

H. Wysor—Metallurgy (1914). Chapters XXIV and XXV for the metallurgy of zinc and mercury.

Rogers—Industrial Chemistry. Chapter XIV describes the manufacture and uses of zinc oxide. See also the references to Chapter XXXVII of this text for references on paints.

Franklin—American Chemical Journal, **47,** 285 (1912) on liquid ammonia as a solvent and ionizing medium.

General References cited in Chapter XXXII of this text.

CHAPTER XXXVI

ALUMINIUM AND OTHER ELEMENTS OF THE THIRD GROUP

Most of the elements of the third group of the periodic system are relatively rare; they are therefore little used and seldom encountered in chemical work. In the outer group, boron is fairly abundant. Its properties have been described briefly in connection with those of silicon, for, like other elements occupying the first place in an outer group, it resembles the elements of the following group more closely than those of the group to which it belongs. Aluminium is widely distributed and extensively used. For these reasons it will receive more extended discussion below. Scandium and yttrium are relatively rare. The former is of interest because its existence and properties were predicted from the periodic system by Mendeléeff before the element was discovered.

The elements from lanthanum to lutecium constitute a group of exceedingly rare substances, called the **rare earth** metals, for which no thoroughly satisfactory position has been found in any form of the periodic system. In the Harkins table, they are arranged on a special loop of the outer helix, but are all placed on the column of the third group. This is done to indicate that the valence of the elements in most of their compounds is three positive. The elements are so similar in properties that their separation and purification is extremely difficult. It would, of course, be of considerable theoretical interest to be able to explain why these elements do not fall in line with the regularities of the periodic system, that is, to explain why, in spite of regularly increasing atomic weight, the valence and other properties remain so nearly constant.[1]

[1] Among the elements which fit into the periodic system, the nuclei of the atoms of any element of a series have positive charges one greater

The inner group consists of the elements gallium, indium and thallium, all of which are rare. They are in many respects similar to aluminium, but seem to be somewhat less electropositive. The valence of the elements is variable; gallium three positive, indium one, two and three positive, and thallium one and three positive. Thallium differs most markedly from the others of the group; thallous hydroxide is a strong base, and the thallous compounds are, in general, more stable than those in which the valence of thallium is three.

Aluminium

Aluminium is too active an element to exist free in nature, but it is found in a great variety of compounds. The felspars of which the compound, $KAlSi_3O_8$, is an example, micas like $KAlSiO_4$, and kaolin (clay) $H_2Al_2(SiO_4)_2 \cdot H_2O$, are its most common minerals. The free metal cannot be readily prepared from these; for this purpose bauxite, $Al_2O_3 \cdot 2H_2O$, and cryolite, $3NaF \cdot AlF_3$, are used.

Preparation of the Metal.—Aluminium is so electropositive that reduction of its compounds to the free metal by chemical means is not feasible. Nor can it be obtained by electrolysis of aqueous solutions of its salts. Hydrogen is liberated so much more readily than aluminium that electrolysis of a salt like aluminium chloride in water yields only hydrogen at the cathode. Difficulties are also encountered in preparing aluminium by electrolysis of fused aluminium compounds; the oxide has too high a melting point, the chloride volatilizes before it melts, and most of the non-volatile common salts either decompose when heated or do not fuse. It is therefore not surprising that early efforts to prepare the element were unsuccessful. In 1890

than those of the atoms of the preceding element; they have also one more electron in the outer zone or shell of the atom. It has been suggested that among the rare earths, the nuclear charge also increases by one from one element to the other, but that the corresponding extra electron is contained in an inner zone of the atoms. Since the chemical properties of the elements are determined almost entirely by the arrangement of the outermost zone, elements constituted as has been suggested for the rare earths should be very similar.

aluminium was a curiosity; today it is one of the most widely used metals. This change was brought about by C. M. Hall's discovery in 1886 that electrolysis of aluminium oxide, dissolved in molten cryolite, is a workable method of obtaining the free metal.[1]

In carrying out the process, a rectangular iron box, lined with a compressed and baked mixture of coke and tar, is used. The lining acts as the cathode; the anodes are a series of carbon rods. Arcs struck by the carbon rods melt the cryolite, and the resistance of the resulting electrolyte to the passage of the current gives enough heat to keep the mass molten. Aluminium oxide is then added to the liquid. The temperature (1000°) is sufficient to melt the aluminium formed at the cathode; the molten metal which sinks to the bottom is tapped off from time to time. Oxygen is liberated at the cathode; it either escapes as a gas or unites with the carbon to form carbon monoxide. As the process continues, the aluminium oxide is replenished in order to keep the solution at its original concentration. It is essential to use very pure materials since the metal cannot readily be purified after it has been prepared. Elaborate plants are required for this purpose because natural bauxite contains various harmful impurities.

Bauxite, after being roasted to oxidize ferrous oxide, is dissolved in concentrated sodium hydroxide solution by heating the mixture under pressure. The resulting solution of sodium aluminate is then cooled and diluted. The addition of a small amount of granular aluminium hydroxide causes the dissolved oxide to precipitate out of the diluted solution in a hydrated, readily filterable, and very pure condition. The remaining solution is concentrated and used to dissolve fresh bauxite, while the precipitated material is converted into aluminium oxide by ignition.

The metal is now widely used for a variety of purposes. On account of its lightness (density = 2.6) it finds employment

[1] A few months after the invention of this method by Hall, a Frenchman, P. L. T. Heroult, made the same discovery without knowledge of Hall's work. Such incidents are of frequent occurrence, and show that inventions of chemical processes are as much the outgrowth of fundamental scientific research as of the genius or inventiveness of individuals.

in the construction of automobiles, airplanes and dirigibles. It is an excellent conductor of electricity, even better than copper (when comparison is made between equal weights of the two metals), and is therefore used for the transmission of electricity. With copper it forms the alloy, aluminium bronze, which possesses high mechanical and chemical resistance; its alloy with magnesium, magnalium, is widely used because it is particularly adapted to working on lathes. Aluminium is also extensively employed in the manufacture of cooking utensils. Large quantities of the metal are used in the making of steel; the aluminium unites with the gases dissolved in the molten steel and thus prevents the formation of blowholes in the ingots. The manufacture of aluminium paint, prepared by mixing the powdered metal with some oily material, may also be mentioned.

Chemical Properties of Aluminium.—In its chemical behavior, aluminium displays a number of interesting anomalies. In agreement with its position in one of the first groups of the periodic system, it is a decidedly electropositive element. Thus, its oxide cannot be easily reduced by chemical means; it readily displaces hydrogen from acids; it reduces oxides of metals such as iron to the free metals with the evolution of large amounts of heat. In spite of its activity in these respects, aluminium may be exposed to air and to moisture without undergoing any apparent change, and may even be boiled with dilute solutions of weak acids without corrosion. On this account it can be used for cooking utensils. The only satisfactory explanation of its apparent inactivity is that it reacts with oxygen to form a very firmly adhering, transparent film of oxide which protects the metal from further attack.

Aluminium Hydroxide.—Thus far in the discussion of the various elements, it has been found that, in general, the hydroxides of strongly electropositive elements are strong bases, and that the strength of the hydroxides decreases as the electropositive character becomes less decided. Slightly electropositive elements like antimony form hydroxides which have both acidic and basic properties. Although aluminium is rather strongly electropositive its hydroxide has not only very weak basic, but actually also acid properties. It may be mentioned that aluminium is

not the only positive element the hydroxide of which behaves in this way. Zinc, chromium, tin and lead, which are fairly electropositive metals, although not so electropositive as aluminium, also have **amphoteric hydroxides,** that is, hydroxides possessing both acid and basic functions.

Aluminium hydroxide, although but very slightly soluble in water, dissolves readily in solutions of both strong acids and of strong bases, thus demonstrating that the substance acts both as a base and as an acid. The solid hydroxide in contact with water is in equilibrium with the dissolved molecules and with their ions, as shown in the following equations, the first of which represents the behavior as a base, and the second the behavior as an acid:

$$Al(OH)_3\downarrow \rightleftarrows Al(OH)_3 \rightleftarrows Al^{+++} + 3OH^-$$

and

$$Al(OH)_3\downarrow \rightleftarrows Al(OH)_3 \rightleftarrows AlO_2^- + H^+ + H_2O$$ [1]

Strong acids dissolve aluminium hydroxide because their hydrogen ions unite with the hydroxide ions of the aluminium hydroxide, acting as a base, and thus drive the first reaction to the right. The resulting solution contains the ions of the **aluminium salt** of the acid used, for example aluminium chloride, $AlCl_3$. On the other hand, strong bases like sodium hydroxide also dissolve aluminium hydroxide because their hydroxide ions unite with the hydrogen ions resulting from the ionization of aluminium hydroxide as an acid. Hence, the second reaction proceeds to the right. In this case, the resulting solution contains the ions of an **aluminate** of the strong base used, for example, sodium aluminate, $NaAlO_2$.

Aluminium salts, even those of strong acids like hydrochloric or nitric, are extensively hydrolyzed, and give strongly acid reactions in aqueous solutions. This shows that aluminium hydroxide is a very weak base. Aluminium salts of very weak acids like hydrogen sulfide or carbonic acid are completely

[1] Probably aluminium hydroxide ionizes also into $AlO_3^{\equiv}$ and $3H^+$, but as usual in such cases, the primary ionization is the most extensive. Likewise ionization into $Al(OH)_2^+$ and OH^- probably precedes complete dissociation when the substance acts as a base.

hydrolyzed. For this reason, the addition of ammonium sulfide or of ammonium carbonate to aqueous solutions of aluminium salts leads to the precipitation of the hydroxide rather than that of the sulfide or carbonate:

$$\begin{cases} Al_2(SO_4)_3 + 3(NH_4)_2S \rightleftarrows Al_2S_3 + 3(NH_4)_2SO_4 \\ Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2S\uparrow \end{cases}$$

and

$$\begin{cases} 2AlCl_3 + 3(NH_4)_2CO_3 \rightleftarrows Al_2(CO_3)_3 + 6NH_4Cl \\ Al_2(CO_3)_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2CO_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \hookrightarrow 3H_2O + 3CO_2\uparrow \end{cases}$$

It is obvious that the removal of aluminium hydroxide as a precipitate, and of hydrogen sulfide and carbon dioxide as gases favors completion of the reactions.[1]

Although aluminium hydroxide is a very weak base, it is an even weaker acid. Its salts with strong bases, such as sodium or potassium aluminate, $NaAlO_2$ or $KAlO_2$, are almost completely hydrolyzed except in the presence of an excess of sodium or potassium hydroxide. Salts of even moderately weak bases, such as ammonium hydroxide, cannot be prepared in solution because they are completely hydrolyzed. For this reason the addition of ammonium chloride to a solution of sodium aluminate causes precipitation of the hydroxide according to the equations:

$$\begin{cases} NaAlO_2 + NH_4Cl \rightleftarrows NaCl + NH_4AlO_2 \\ NH_4AlO_2 + 2H_2O \rightarrow Al(OH)_3\downarrow + NH_4OH \end{cases}$$

Aluminium hydroxide is relatively unstable. It loses water to form the oxide when heated to only moderately high temperatures, although it may be kept unchanged under ordinary conditions. The oxide thus formed is soluble in acids and bases,

[1] It is not necessary to assume the intermediate formation of the carbonate and sulfide of aluminium in these reactions. These substances are salts and therefore highly ionized and only the ions are involved in the reactions. The student should write the equations from this point of view. Attention may also be called to the fact that because of hydrolysis ammonium sulfide and carbonate exist in solution largely as the corresponding acid salts.

but when it is heated above 800°, it becomes insoluble in all ordinary solvents.

The hydroxide (formed by hydrolysis of the acetate) is used in waterproofing delicate fabrics, and in rendering cotton and linen non-absorbent. The oxide, in the form of corundum and emery, is used as an abrasive. Alundum is made by barely melting the oxide in an electric furnace; it is used as a refractory material for crucibles. Rubies and sapphires are crystallized varieties of the oxide which owe their color to traces of impurities.

Aluminium Sulfate and the Alums.—Bauxite dissolves in concentrated sulfuric acid. From the solution, the hydrate of aluminium sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, is deposited on cooling. If an amount of potassium sulfate equivalent to the dissolved aluminium sulfate is added to the solution before crystallization takes place, the double salt,[1] $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, frequently called potassium or potash **alum,** crystallizes out. In place of potassium sulfate, the sulfate of any one of the alkali metals or of ammonium may be used, thus giving rise to other alums, such as soda alum; these have formulae entirely analogous to that of potassium alum. On the other hand, the aluminium in the alum may be replaced by other metallic elements, such as chromium or iron, which are trivalent in their sulfates.[2] All of the alums yield octahedral crystals.

Aluminium sulfate and the alums are extensively used for a variety of purposes. The use of the sulfate as a mordant in dyeing and in coagulating colloidally suspended material in water supplies has already been mentioned (see page 441). In water purification, the coagulating effect of the ions of the salt is not the only important function. The carbonates present in the water precipitate aluminium hydroxide in gelatinous form which adsorbs finely divided suspended material, and thus brings about more rapid settling. If the water to be purified contains no carbonates, lime is added to bring about the formation of the hydroxide. The use of aluminium sulfate in making paper sizing also depends on the formation of the hydroxide.

[1] See page 511.

[2] An alum which contains chromium in place of aluminium, is called a chrome-alum; one which contains trivalent iron, a ferric alum, and so on.

Since the alums are more easily purified, especially from iron, than is the simple sulfate, they are employed in place of the latter when the highest degree of purity is required, as for example in baking powders. The function of a baking powder is the liberation of carbon dioxide in order to make the dough porous. For the reasons given on page 535, a mixture of soda alum and a carbonate liberates carbon dioxide as soon as it becomes moist. The importance of aluminium silicates is discussed on page 454.

Comparison of Aluminium with the Elements of the Preceding Groups.—The behavior of aluminium and its compounds shows that the element is decidedly less electropositive than the elements of either the alkali metal or alkaline earth groups. The metal is less readily attacked by oxygen or by water than are the others mentioned. It is a less vigorous reducing agent as shown by the facts already cited, and by its action with nitric acid, with which it yields only traces of hydrogen, although it does effect reduction to ammonium nitrate. Its hydroxide is a much weaker base and is more readily decomposed into the oxide than are the alkali or alkaline earth hydroxides. Its valence is exclusively three positive. It is, on the other hand, far more electropositive than the metals of the two preceding inner groups—the copper and the zinc groups. This is demonstrated by the following facts: (1) the oxides of these elements are vigorously reduced by aluminium to the free metals; (2) aluminium reacts more rapidly than they with dilute acids; (3) aluminium salts like the nitrate and sulfate are more stable toward heat. Like the elements of the first two outer groups and unlike those of the corresponding inner groups, it shows no tendency to form stable complex ions, nor to take up electrons and act as an oxidizing agent. Its salts are somewhat similar in solubility to those of magnesium, but this statement must be taken merely as a rough comparison. Aluminium differs strikingly from all of the outer group elements mentioned above in forming an hydroxide which is both very weakly basic and acidic. In this respect it resembles zinc somewhat, but zinc hydroxide is a far stronger base than aluminium hydroxide, in spite of the fact that zinc is a less electropositive element.

EXERCISES

(1) Review the chemistry of boron by showing in what respects it is more like silicon than like aluminium. In what respect is it like aluminium?

(2) How do the rare earth elements depart from the regularities of the periodic system?

(3) Explain why a special method had to be devised for the manufacture of aluminium.

(4) Make a schematic drawing for apparatus in which aluminium could be prepared. Describe the changes occurring at the cathode and at the anode.

(5) (*a*) Why is it surprising that aluminium is not readily tarnished in air? How is the fact explained? (*b*) What is the evidence that aluminium is an active metal?

(6) What is the experimental basis for the statement that aluminium hydroxide is both an acid and a base? Write the formulae of salts formed by aluminium hydroxide acting as a base, and of salts formed by its action as an acid.

(7) (*a*) How may it be proved experimentally that aluminium hydroxide is a very weak base? (*b*) Answer the same question for aluminium hydroxide as an acid.

(8) (*a*) Explain why the addition of sodium carbonate to an aqueous solution of an aluminium salt causes the formation of aluminium hydroxide. (*b*) Write the equation for the reaction from an ionic point of view.

(9) Explain why, although aluminium hydroxide is both an acid and a base, it does not neutralize itself. (Take into consideration the fact that aluminium hydroxide is both a very weak base and a very weak acid, and very insoluble as well.)

(10) What is an aluminate?

(11) (*a*) In what ways do double salts differ from salts of complex ions? (*b*) What are the ions contained in a solution of soda alum? What is the formula of potassium chrome-alum and what are the ions present in its solution?

(12) Explain the function of aluminium sulfate (*a*) in dyeing and (*b*) in the settling of impurities in water.

(13) Explain how an alum baking powder works. Assume that the baking powder consists of soda alum and sodium bicarbonate.

(14) (*a*) Point out in what respects aluminium is like the alkali and alkaline earth metals, and in what respects it differs from them. (*b*) Compare aluminium with zinc.

(15) Explain how and why aluminium may be used in the preparation of other metals. (See page 464 under aluminothermy.)

(16) Suggest methods of preparation of the following aluminium salts: chloride, phosphate, sulfide, nitrate.

REFERENCES

PRING—The Electric Furnace (1921). Pages 356–367 for the manufacture of aluminium.

STEWART—Recent Advances in Physical and Inorganic Chemistry (1919). Chapter X for a brief discussion of the rare earths.

The General References cited in Chapter XXXII of this text and the Special References in Chapter XXX.

CHAPTER XXXVII

THE METALLIC ELEMENTS OF THE FOURTH GROUP, TIN AND LEAD

In the Harkins form of the periodic table the fourth group is separated into two divisions. The first, containing titanium, zirconium, cerium, etc., marks the point at which the helix turns to the inner series; the second, which contains germanium, tin and lead marks the return of the helix to the outer series. In a sense, therefore, the Harkins arrangement does not classify either subdivision of the group as belonging strictly to outer or inner series. In many respects germanium, tin and lead are more closely related to silicon and carbon than are the other elements of the group.[1] For example, germanium forms several hydrides similar to those of silicon, and tin and lead each form very unstable gaseous hydrides in which the valence of the elements in question is four. The elements in the column beginning with titanium, although capable of dissolving hydrogen to a limited extent, form no compounds with it. Germanium, tin and lead are bivalent or quadrivalent in their compounds, and are similar to carbon in this respect for it, also, is bivalent in a few of its compounds.[2] In the other subdivision the valences are more irregular; all of the elements are quadrivalent, but titanium is also bivalent or trivalent in a number of compounds and cerium is trivalent in a series of salts.[3] The elements of both

[1] Titanium, however, resembles silicon quite closely in the behavior of its oxide, the hydroxide, the nitride and other compounds.

[2] In the oxides Pb_2O_3 and Pb_3O_4 two kinds of lead ion are probably present, for these compounds may be considered to be $Pb \cdot PbO_3$ and $Pb_2 \cdot PbO_4$ respectively.

[2] In some arrangements of the periodic table, cerium is grouped with the rare earths, which it resembles in many ways.

subdivisions are more electropositive than either carbon or silicon, for all of them are metallic. Furthermore, with increase in atomic weight the elements appear to become more electropositive as shown by the increasingly basic character of their hydroxides. Carbonic acid has no basic properties; silicic acid, though neither strongly acidic nor basic is decidedly more acidic than basic; the hydroxides of quadrivalent tin and of quadrivalent lead are likewise more acidic than basic, but the hydroxides in which these elements are bivalent are more basic than acidic. In the other subdivision, cerium and thorium hydroxides are exclusively basic.

Titanium is used in steel manufacture. The addition of small amounts of titanium increases the durability and the toughness of the steel. Zirconium compounds are used in the manufacture of incandescent mantles, and in the preparation of very refractory materials. The most important use of thorium and cerium is likewise in incandescent mantles.[1] A mantle consisting of a mixture of 98 to 99 per cent of thorium oxide and 2 to 1 per cent of cerium oxide gives the maximum luminosity; slight variations from these proportions enormously reduce its efficiency. Cerium has a great tendency to unite with oxygen; an alloy of the metal with 30 per cent of iron catches fire in the air when it is scratched with a file and thus broken up into minute fragments. This property is used in gas- and cigar-lighters. Tin and lead are far more important than the other metals of the group; they are discussed more fully below.

Tin and Lead

Occurrence and Extraction.—Both tin and lead were well known to the ancient Egyptians, and probably to earlier civilizations. This is unquestionably due to the fact that both metals are rather readily manufactured from their ores. Tin is found chiefly in tinstone or cassiterite, SnO_2, which is easily reduced by carbon (coal) to the free metal. Before reduction, the ore

[1] Thorium, as has been mentioned on page 349, is a radio active element. One of its products of disintegration is meso-thorium which is used to replace radium in the manufacture of luminous paints. The more active disintegration products are also used medicinally.

is purified by washing and roasting; the free metal obtained by reduction is further purified by remelting it, and allowing it to flow away from the more difficultly fusible impurities. The most important deposits of the ores are in the East Indies, Bolivia and England.

Galena, PbS, is the most important lead ore. Rich ores are roasted until a part of the sulfide has been converted into the oxide and sulfate. The air supply is then cut off and the temperature raised; under these conditions lead is produced according to the following equations:

$$PbS + 2PbO \rightarrow 3Pb + SO_2$$

$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$$

Ores not so rich in lead are reduced by being heated with scrap iron or with iron ore and coke. Lead is refined electrolytically by the Betts process.

Physical Properties and Uses of the Metals.—Both of the metals have relatively low melting points, that of tin being 232° and that of lead 327°. Both have low tensile strength, but are very malleable; tin especially can be beaten or rolled into very thin sheets (tin foil). Tin is silvery white and moderately soft; it tends to form fairly large crystals. Lead is soft and gray in color.

An unusually interesting example of allotropic modifications is found in the case of tin. Medallions, commemorative of historic occasions, were formerly quite frequently struck off in tin and kept in museums. It was discovered that these medallions occasionally disintegrated into a gray powder. A similar phenomenon has been observed in tin organ pipes and in blocks of the metal kept for storage. One of the curious facts about the phenomenon is that the tendency to undergo the disintegration seems to be "contagious"; objects in which no sign of the change is visible soon show evidences of it after they are placed near one in which the change has begun. On this account the transformation is called the "tin pest." Careful investigation has led to the discovery that tin exists in two allotropic modifications: white tin stable above 18°, and gray tin stable below

this temperature. An object, made of white tin, may, however, be cooled below the transition point without undergoing noticeable change, because the reaction is ordinarily slow, and because white tin seems to be capable of existing for a long time in a metastable condition below 18°. If, however, the white tin at temperatures below 18° is brought into contact with even a minute particle of the gray variety, the transformation begins, and slowly progresses through the whole object. The effect of the gray tin is like that of a small particle of the solid material added to a supersaturated solution or a supercooled liquid.

Tin is not readily attacked by either air or water, and is therefore used in utensils which require these properties. Tin pipes are used in apparatus for making beverages which might attack iron or lead pipes, and in scientific laboratories to carry the supply of distilled water. For most purposes, objects made of massive tin are too expensive. Other metals are therefore coated with it. Tin plate is made by dipping sheets of steel into molten tin, and is used in making "tin" cans. Copper vessels are often lined with tin for use as cooking utensils. Although tin is in many respects a less active metal than iron, the former is attacked by dry chlorine while the latter is not; this fact is the basis of the Goldschmidt process for detinning scrap tin plate. Tin is used extensively in the making of alloys such as **bronze** (3–8 per cent tin, 11 or more per cent of zinc, copper and a little lead), **soft solder** (50 per cent each of lead and of tin), and **pewter** (25 per cent lead).

Lead also is not readily attacked by air, but it is somewhat more readily dissolved by water than is tin. Nevertheless it was formerly much used for water pipes, in spite of the fact that the metal and its compounds are very poisonous. In most instances its use in pipes is safe because most waters are hard enough to form strongly adherent, insoluble deposits of lead carbonate and sulfate which protect the water from contamination. Nowadays lead pipe is much less used for this purpose than formerly. Since iron pipe and fittings are obtainable everywhere they make the more expensive lead unnecessary. It is still used, both as pipe and sheet, in chemical factories, because

it interacts so slowly with many reagents, or becomes covered with protective coatings. It is, for example, the best material with which to line vessels in which dilute or moderately concentrated sulfuric acid is to be used, because the coating of lead sulfate protects the metal from further action of the acid. Since lead sulfate dissolves in concentrated sulfuric acid (giving the acid sulfate), lead lined vessels cannot be used to hold the concentrated acid (above 77 per cent), and iron vessels, which are acted on by dilute sulfuric acid but not by concentrated, are employed. Lead pipe is used also in covering electric cables; its resistance to the action of air and water and its pliability make it particularly useful for this purpose. Large quantities of the metal and its oxides are used in storage batteries. Its alloys with tin have already been described; type metal, which contains 20–25 per cent of antimony, is another very important alloy of lead. It is harder than pure lead and expands when it cools; hence it gives a perfect reproduction of the mold. Lead compounds are used in a great variety of ways—in glass and enamel, in certain kinds of plumbers' cements, and very extensively in paints.

Chemical Properties of the Metals and of their Ions.—Both of the metals are moderately active; they are far less electropositive than the alkali and alkaline earth metals, but more electropositive than those of the copper group. They act slowly with moderately dilute solutions of strong acids to liberate hydrogen, and are slowly oxidized by air. Tin, however, does not tarnish appreciably, possibly because of the formation of a coating of oxide. They do not reduce nitric acid as completely as do the more active metals; with dilute acid the *chief* products are nitrogen, nitrous oxide, or nitric oxide, depending upon the temperature and the concentration of the acid, while with the concentrated acid nitrogen tetroxide is obtained.[1] Tin, in the presence of acids, is often used especially in organic chemistry as a mild reducing agent. Since both elements form hydroxides which may function as acids, they are both attacked by strong bases, yielding hydrogen.

[1] The metals reduce a small fraction of the dilute nitric acid to ammonium nitrate.

Both elements form two kinds of positive ions in which they are, respectively, two and four positive. For tin the tendency to be four positive predominates. Thus the black oxide, SnO, obtained by the decomposition of stannous oxalate, burns in air to give the dioxide. Stannous chloride, by virtue of its considerable tendency to go over into stannic chloride, is an active reducing agent. An illustration of this property is its reaction with mercuric salts. (See page 527.)

With lead conditions are reversed and the bivalent ion is the more stable. Thus lead dioxide is a strong oxidizing agent because the quadrivalent positive lead ion tends to take on 2 electrons to become bivalent. Lead tetrachloride spontaneously loses chlorine at ordinary temperatures, and is, in fact, a dangerous compound to handle because the decomposition may occur explosively. In complex ions, such as $PbCl_6^{=}$, lead with the valence number four positive is more stable than in the simple ions; this is analogous to the fact that complex cuprous salts are more stable than the simple ones, and the explanation is the same for the two cases (see pages 512–513).

In general the salts of tin are more soluble than those of lead; the halides and the sulfates of tin are soluble whereas lead sulfate is very slightly soluble and lead halides are dissolved appreciably only by hot water. Sulfates, nitrates and carbonates of both metals are rather readily decomposed to the oxides by heat.

Oxides of the Elements.—Tin forms **stannous** and **stannic oxide,** SnO and SnO_2. The former has already been sufficiently described. Stannic oxide, found in nature as tinstone, is obtained in purer form by heating the metal with concentrated nitric acid. The first product of the reaction is probably stannic nitrate which is almost completely hydrolyzed, giving a hydrated form of stannic oxide usually called stannic acid:

$$Sn + (4 + 4)HNO_3 \rightarrow Sn(NO_3)_4 + 4NO_2 + 4H_2O$$

$$Sn(NO_3)_4 + 3H_2O \rightarrow 4HNO_3 + H_2SnO_3\,[1]$$

[1] The formula H_2SnO_3 is usually assigned to the hydrated oxide because salts such as Na_2SnO_3 may be obtained from it. It is likely, however, that the oxide takes on more than 1 molecule of water, and it is impossible to determine what the exact formula is or whether a single formula can correctly represent the behavior of the substance. (See below.)

The pure oxide is then obtained by heating the stannic acid. If the temperature used is relatively low, the oxide is soluble in acids, but if ignition is carried out at high temperatures a very inert mass results. The oxide is white when cold, yellow when hot.

Lead forms a much larger number of oxides. **Litharge,** PbO, which is yellow, is obtained by oxidation of lead in air during Parke's process for the manufacture of silver or by heating any of the other oxides of lead above 600°. **Lead dioxide,** which is brown, is usually obtained by oxidizing sodium plumbite with bleaching powder:

$$Na_2PbO_2 + Ca(OCl)Cl + H_2O \rightarrow 2NaOH + CaCl_2 + PbO_2$$

It is not formed, as is the corresponding oxide of tin, by action of concentrated nitric acid on the metal. The dioxide is an active oxidizing agent as has been shown in various connections. Its chief use, however, is in the manufacture of storage batteries. **Minium** or **red lead,** Pb_3O_4, may be considered a lead salt of plumbic acid as indicated by the formula, $Pb_2 \cdot PbO_4$. This interpretation is borne out by its reaction with nitric acid:

$$Pb_2PbO_4 + 4HNO_3 \rightleftarrows 2Pb(NO_3)_2 + H_4PbO_4$$

The hypothetical plumbic acid loses 2 molecules of water yielding lead dioxide. Red lead is prepared by heating litharge or basic lead carbonate in air at about 475°. It is used in glass, in glazes for pottery, and in paints. The monoxide is likewise used in glass making; when mixed with glycerine it gives a cement for glass or similar materials.

The **trioxide,** Pb_2O_3, and the **suboxide,** Pb_2O, are less important compounds. The former is prepared by oxidizing the monoxide in alkaline solution, and is, like red lead, a compound of bivalent and of tetravalent lead, $Pb \cdot PbO_3$. The suboxide is prepared by gentle heating of the oxalate of lead.

The Hydroxides and Oxygen Acids of Tin and of Lead.— Stannous and lead hydroxides are both amphoteric electrolytes. They therefore give rise to two series of salts. The hydroxide is the base from which the salts of one series are derived; and in the formation of the other series the hydroxide functions as an

acid. Thus stannous hydroxide reacts with hydrochloric acid to give **stannous chloride**:

$$Sn(OH)_2 + 2HCl \rightleftarrows SnCl_2 + 2H_2O$$

and with sodium hydroxide to give sodium **stannite**:

$$Sn(OH)_2 + 2NaOH \rightleftarrows Na_2SnO_2 + 2H_2O$$

Stannous hydroxide is a weak base and a weaker acid; both types of salts are therefore extensively hydrolyzed in aqueous solution. Lead hydroxide is a stronger base, somewhat of the order of cupric hydroxide, and a weaker acid. **Lead** (plumbous) **salts** are therefore less hydrolyzed while **plumbites** are more extensively hydrolyzed than the corresponding tin compounds.

When an aqueous solution of stannic chloride is treated with ammonium hydroxide a gelatinous precipitate is obtained. From analogy with similar cases this material should consist of stannic hydroxide, $Sn(OH)_4$, and since it appears to be essentially acid in character its formula might also be written H_4SnO_4. But when the precipitate is redissolved in sodium hydroxide the salt Na_2SnO_3 is obtained. This fact led to the assumption that the gelatinous precipitate probably goes over, by loss of 1 molecule of water, to H_2SnO_3. But even this assumption is unwarranted, because when the precipitate is exposed to dry air it loses water gradually until SnO_2 is left and neither H_4SnO_4 nor H_2SnO_3 is obtained. The free acid of which the **stannates** such as Na_2SnO_3 may be considered derivatives does not exist. The precipitate described above must be looked upon as stannic oxide, which, like freshly precipitated silicon dioxide, is capable of holding varying amounts of water by adsorption. The properties of the hydrated dioxide depend very largely upon the size of its grains. Thus the oxide obtained by heating tin with concentrated nitric acid is not nearly so readily attacked by either acids or alkalies as is the form precipitated by ammonium hydroxide from solutions of stannic chloride. The differences are so great that chemists once thought that two definite stannic acids, alpha and beta acids, existed. It is now fairly certain that the differences are all due to particle size and amount of adsorbed water. These differences are not sharp, since all gradations between the two extreme types have been prepared.

Stannic hydroxide is decidedly more acid than basic, and the same is true of **plumbic hydroxide.** The latter, like stannic hydroxide, has not been isolated, but **plumbates** such as Na_2PbO_3 are known. Both stannates and plumbates are hydrolyzed, showing the corresponding acids to be relatively weak. But they are hydrolyzed less extensively than the salts of silicic acid. This fact is unexpected; since tin and lead are more electropositive than silicon, the hydroxides of the latter elements should be less acid and more basic than those of silicon. The discrepancy has been explained on the assumption that the stannates and especially the plumbates are complex salts, which do not really correspond to the simple formulae assigned to them.

Salts of the Group.—Stannous salts are used chiefly as reducing agents; the chloride is the most important. Stannic compounds possess little salt like character. Thus stannic chloride may be dissolved in water; the resulting solution is a very poor conductor of electricity showing that the chloride is little, if at all ionized. The conductivity of the solution gradually increases, due to slow hydrolysis of the chloride which results in the formation of hydrochloric acid. Plumbic chloride (lead tetrachloride) is similar to stannic chloride in this respect. These chlorides are therefore closely analogous to silicon tetrachloride, which is also not salt like, and somewhat like the halides of carbon, except that hydrolysis of the latter is slow even at elevated temperatures. Stannic compounds are used as mordants. In addition to the lead salts already mentioned, the basic carbonate, white lead, $Pb_3(OH)_2(CO_3)_2$, and lead sulfate are used in enormous quantities in paint manufacture. Other lead salts also are used in the same way.

EXERCISES

(1) In what respects do the elements of group IVB resemble carbon and silicon more closely than do the elements of group IVA?

(2) In the methods for obtaining lead from the poorer ores, what is the evidence to show that this element is less electropositive than iron?

(3) Suppose a sample of crude lead contains zinc and silver as impurities. What would become of each of the metallic impurities during an electrolytic process of refining?

(4) (*a*) Explain why the "tin pest" appears to be "contagious." (*b*) Under what conditions is each of the modifications of tin metastable?

(5) Explain why lead pipes may be used to carry water supplies only if the water contains sulfates or carbonates.

(6) Write the equation for the reaction of concentrated sulfuric acid on lead sulfate, and explain why this acid cannot be kept in lead-lined vessels.

(7) What is the basis for the statement that tin and lead are less active than the alkaline earth group metals and more active than the metals of the copper group?

(8) Are tin and lead more or less electropositive than zinc? State all of the facts which enable you to form an opinion on this question.

(9) (*a*) Write the equation for the reaction of lead on sodium hydroxide. (*b*) Explain why sodium hydroxide reacts with lead to give hydrogen more readily than does water (see page 322).

(10) (*a*) What experimental evidence shows that tin has a greater tendency to be four positive rather than two positive? (*b*) What evidence is there that the reverse is true of lead? (*c*) In view of these facts, should you expect stannic chloride to be more or less stable towards heat than plumbic chloride? (*d*) Write the equation for the equilibrium between plumbous (Pb^{++}) and plumbic (Pb^{++++}) ions. Explain why the formation of a complex ion containing Pb^{++++} should make plumbic compounds more stable than they would otherwise be.

(11) Contrast the reaction of concentrated nitric acid on tin with its action on lead.

(12) What reason is there for believing that minium is a compound containing both bivalent and tetravalent lead?

(13) Write equations for the reactions of lead hydroxide with nitric acid and with sodium hydroxide.

(14) Judging from the behavior of an aqueous solution of stannic chloride, what should one conclude about the strength of stannic hydroxide as a base? Is stannic hydroxide stronger as a base or as an acid? What is the evidence?

(15) Mention the most important uses of tin and of lead.

REFERENCES

Stewart—Recent Advances in Physical and Inorganic Chemistry (1919). Chapter XI for incandescent gas mantles.

H. Wysor—Metallurgy (1914). Chapters XXI, XXII, XXXIII and XXV for the metallurgy of tin and lead.

Rogers—Industrial Chemistry (1921). Chapters XIII, XV and XVI deal with lead compounds and their use in paints.

General References in Chapter XXXII of this text.

CHAPTER XXXVIII

ELECTROCHEMISTRY

CELLS AND BATTERIES.——HYDROGEN ELECTRODE.——SINGLE POTENTIAL DIFFERENCES.—COUPLES.—STORAGE BATTERIES

IN oxidation and reduction some atoms lose and others gain electrons. The same sort of change occurs also in the electrolytic preparation of the halogens, of the alkali and alkaline earth group metals, of aluminium, and of sodium hydroxide, and to the refining of copper. But this preparative side is only one phase of the important subject, **electrochemistry.** Not only are chemical changes brought about by electrical means but, conversely, electrical current may be produced as a result of chemical action. In order to produce current the reactions must be carried out in such a way that the electrons given off by the reducing agent pass through a metallic conductor before they are taken up by the oxidizing agent. Arrangements for accomplishing this result are called cells or batteries.[1]

According to Faraday's law, 1 Faraday of electricity (96,500 coulombs) liberates 1 gram equivalent of any element, or, more generally stated, changes chemically 1 gram equivalent of substance. In order to produce 1 Faraday of electricity the same quantity of material must react. Chemical reactions, however, are characterized, not by the quantity of electricity produced, but by the electrical energy liberated or consumed. The energy is measured in terms of the product: (quantity of electricity) $\times$ (the electromotive force at which the current is delivered). Although the first term of this product, the quantity of electricity, is the same for the interaction of equivalent amounts of any substances, the energy change depends on the nature of the reaction; it follows that various types of batteries or cells, involving differ-

[1] A battery consists of a series of cells.

ent chemical reactions, must each deliver current with a characteristic electromotive force. The value of the latter is usually expressed in volts.

Construction and Operation of a Cell.—Zinc, when dipped into a vessel containing water, sends positively charged ions into solution as a result of the reaction:

$$Zn \rightleftarrows Zn^{++} + 2\epsilon$$

The liberated electrons are retained on the residual metal. The reaction, however, soon ceases because the accumulation of the positive ions in the solution and of electrons on the metal tends to reverse it. Suppose that, in another vessel, a platinum electrode, also dipped into water, is kept saturated with elementary chlorine by continuously passing a stream of the gas through the liquid. Chlorine molecules go over into the ionic condition, as represented by the equation:

$$Cl_2 + 2\epsilon \rightleftarrows 2Cl^-$$

But this reaction must also soon stop, because of the growing concentration of negative ions in the solution and the partial exhaustion of the supply of electrons from the electrode.

In the first vessel the formation of zinc ions is impeded by the presence of electrons on the electrode, and by an excess of positive ions in the solution; in the second vessel formation of chloride ions ceases because of a deficiency of electrons on the electrode, and an excess of negative ions in the solution. But if the 2 electrodes are connected by a metallic conductor, the electrons which accumulate on the zinc, because of the formation of positive zinc ions, flow to the platinum electrode to furnish those required for the formation of negative chloride ions. If, furthermore, the solutions are joined by a tube filled with water, as shown in Fig. 27, the zinc

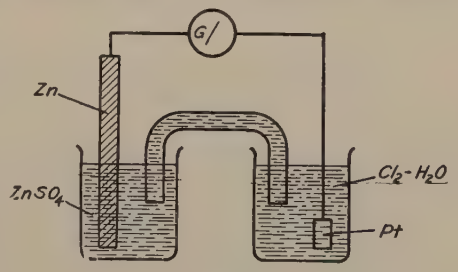


Fig. 27.

ions, too, flow away from the zinc electrode, and the chloride ions from the other. Both of the chemical reactions mentioned above may now proceed to the right because all of the causes which impeded the forward action are removed by making the connection in the way described. The two equations may be combined:

$$Zn + Cl_2 \rightarrow Zn^{++} + 2Cl^-$$

A reaction involving oxidation and reduction is thus carried out in such a way that the electrons, liberated by the reducing agent (zinc), pass through a metallic conductor before being taken up by the oxidizing agent (chlorine). A current of electricity is, therefore, produced. The circuit consists of two parts: the metallic conductor through which the electrons flow, and the liquid through which the ions diffuse. The zinc electrode, at which electrons are liberated, is the negative pole of the cell, and the platinum-chlorine electrode, from which electrons are removed, is the positive pole. The cell described has, however, an enormous internal resistance because the water (which at the beginning of the reaction contains but few ions) is a very poor conductor. This difficulty may be avoided by adding a salt, such as potassium nitrate, to increase the conductivity of the liquid.

Since the cell just described involves a specific chemical reaction, it should, as has already been explained, deliver current at a definite potential difference. This is, however, true only if the reaction is carried out under exactly defined conditions. A large excess of zinc ions in the solution surrounding the zinc rod causes zinc ions and electrons to unite, and thus decreases the electron density on the electrode.[1] The difference between the electron density on the zinc and on the platinum-chlorine electrode is consequently not as great as if the concentration of zinc ions in the

[1] The term electron density is used to indicate what is analogous to a "concentration of electrons" on the electrode. Neither term is accurate. It would be better to discuss the relationship between the "escaping tendency" of the electrons from the electrode and the concentration of the solution, rather than to use the terms employed in the text. It is impossible, however, to give here a description of so complicated a system as a cell without some sacrifice of exactness of statement. The effort has been made to select a terminology which would give a picture by which the behavior of cells may be visualized.

solution were small. Since the electromotive force of the cell may be looked upon as a measure of this difference in electron density, an increase in the concentration of zinc ions must cause a decrease of the electromotive force; a decrease in the concentration of these ions must have the opposite effect. In the same way, increasing the concentration of chloride ions in the vessel containing the platinum-chlorine electrode, or reducing the concentration of gaseous chlorine drives the reaction: $2Cl^- \rightarrow Cl_2 + 2\epsilon$ to the right; either of these changes therefore prevents the passage of electrons into the solution. This effect also decreases the electromotive force of the cell by decreasing the difference in electron density on the 2 electrodes. It follows that *the electromotive force of a cell depends not only on the nature of the reacting substances but also on their concentrations.*

The Daniell Cell.—Nothing was said, in the preceding discussion, about the concentration of the metallic zinc. The density, and therefore the concentration,[1] of solids at constant temperature varies but slightly with changes in external conditions. A cell in which both electrode processes involve only solids and solutions must, consequently, have a more constant electromotive force than one involving a gaseous substance. A cell utilizing only solid electrode materials can be constructed by using for one pole a zinc rod, dipping into a solution containing zinc ions, and a copper rod dipping into a solution of cupric ions for the other. At the zinc rod the reaction taking place again is:

$$Zn \rightleftarrows Zn^{++} + 2\epsilon$$

At the copper rod, the reaction:

$$Cu \rightleftarrows Cu^{++} + 2\epsilon$$

is involved. Since zinc has a much greater tendency than copper to form ions, the density of the electrons on the zinc rod must become greater than on the copper pole, provided the concentration of the ions in the two solutions is the same. A difference of potential is, therefore, created between the two electrodes, when

[1] The relationship becomes clear by recalling that the density is equal to the quotient, weight/volume, and concentration is equal to (weight in gram equivalents)/volume.

they and the two solutions are connected as described for the zinc, platinum-chlorine combination. Electrons are liberated at the zinc rod by the formation of ions; the latter pass into and diffuse through the solution, while the electrons flow from the zinc to the copper electrode. Here they are taken up by copper ions. The equations for the reactions may be combined:

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu$$

This familiar reaction is thus also carried out in such a way that a current of electricity is produced.

In practice, the arrangement for utilizing the reaction between zinc and cupric ions in the production of electrical current is somewhat modified. The smaller the concentration of zinc ions in the solution surrounding the electrode, the greater is the tendency of zinc to ionize, and the greater the resulting density of electrons on the zinc pole; the larger the concentration of cupric ions in the solution surrounding the copper electrode, the greater the tendency of the ions to take up electrons, and the smaller the electron density on the electrode. If, therefore, the zinc rod is dipped into a sodium chloride solution which contains only a trace of zinc ions,[1] and the copper rod into a solution saturated with copper sulfate, the electromotive force of the cell must have a maximum value, because, under these conditions, the difference in the density of the electrons on the two electrodes is as great as it can be. Since the saturated solution of copper sulfate (which may be prepared by dropping crystallized copper sulfate into the sodium chloride solution) is very dense, it stays at the bottom of the vessel. The use of a tube or other device to keep the two portions of the cell separate is therefore not absolutely necessary. The copper electrode (see Fig. 28), with a wire leading upward, is placed in the bottom of a battery jar; the zinc electrode is suspended at the top; the jar is filled with salt solution; and the copper sulfate crystals are thrown in. As soon as the wire from the copper pole is connected with the zinc, the current flows. This arrangement is known as the gravity form of the Daniell cell. Since copper sulfate, in spite of the high density of its saturated solution, never-

[1] As soon as the zinc electrode is dipped into the sodium chloride solution, a few zinc ions must form, so that the solution is never entirely free from them.

less diffuses slowly, copper ions ultimately come into direct contact with the zinc. A part of the material then reacts in such a way that electrons pass directly from metallic zinc to copper ions, without the intervention of a metallic conductor. Consequently a part of the energy of the reaction is liberated as heat instead of electricity. To avoid this loss, a porous partition is used in some forms of the Daniell cell. The flow of ions through this partition, except under the influence of the current itself, is so slow that very little direct action occurs.

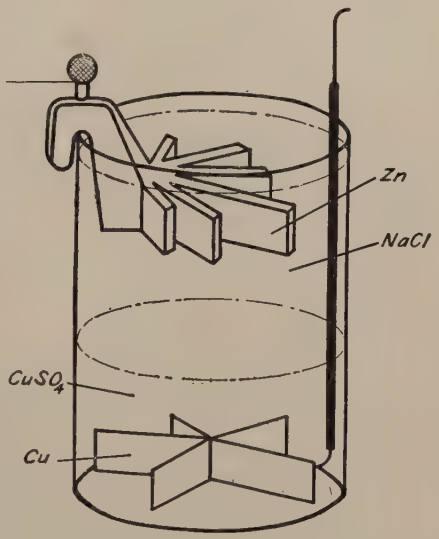


Fig. 28.

The Normal Hydrogen Electrode.—A piece of platinum, kept saturated with hydrogen by passing a stream of the gas through the liquid in contact with the metal, behaves as if it were an electrode of elementary hydrogen. Hydrogen molecules, by loss of electrons, go over to hydrogen ions in the reversible reaction:

$$H_2 \rightleftarrows 2H^+ + 2\epsilon$$

In order to saturate the electrode with the gas and attain equilibrium between elementary hydrogen and its ions as rapidly as possible, the electrode is usually coated with a deposit of finely divided platinum (platinum black), which has a very much greater surface than the massive metal. Such an electrode, saturated with hydrogen at atmospheric pressure, and dipping into a solution containing 1 gram equivalent of hydrogen ion per liter (a normal hydrogen ion solution), is called the normal hydrogen electrode. Some of its important applications are described below.

Single Potential Differences. The Electromotive Series.—Measurements may be made of the electromotive forces of cells

consisting of a normal hydrogen electrode connected with electrodes of other elements. When these other electrodes dip into solutions normal with respect to the ions of the element in question, the values of the electromotive force are called the **single potential differences** of the elements (in terms of the normal hydrogen electrode). They represent the relative tendencies of these elements to form ions, and put into exact numerical terms the information contained in the **electromotive series.**

The precise meaning of the data contained in the following table of single potential differences is made clear by a few illustrations. Zinc has a much greater tendency than hydrogen to form ions. Consequently, in a cell consisting of a normal hydrogen electrode and of a zinc electrode in a normal zinc ion solution, zinc sends ions into solution. The electrons thus liberated flow from the zinc to the hydrogen electrode, and there discharge hydrogen ions. The electromotive force of the cell at room temperature is 0.76 volt. Since the zinc electrode is the source from which the electrons flow, it is the negative pole; in the table, a minus sign is therefore placed before the number 0.76 for the single potential difference of zinc. Hydrogen, on the other hand, has a greater tendency than copper to form ions. In a cell consisting of a normal hydrogen electrode and a copper electrode in a normal cupric ion solution, the hydrogen sends ions into solution and cupric ions are deposited. The copper is the positive pole of the cell, as is indicated in the table by placing a plus sign before the number 0.34, which is the difference of potential of the copper-hydrogen cell. When a hydrogen electrode is combined with a chlorine electrode, both elements send ions into solution, but the hydrogen ions are positive and the chloride ions negative. Hence the hydrogen electrode is negative because of the electrons liberated at its surface, and the chlorine electrode is positive because it must give up electrons. The single potential of chlorine carries the prefix + to indicate these facts.

According to this scheme for assigning + or − prefixes to the values in the table the most electropositive elements have the largest negative single potentials and the most electronegative elements the largest positive single potentials. Confusion which might result from this method of stating the experimental results

is avoided by keeping in mind (1) that the values given are all in terms of the hydrogen electrode and are not absolute values; and (2) that the negative sign before the single potential difference of an element simply means that it gives up electrons more easily than hydrogen, and the positive sign that the element either loses electrons less readily than hydrogen or that it takes them up.[1]

TABLE XXV

ELECTROMOTIVE SERIES

Single Potential Differences in Volts of Some of the Elements with Reference to the Normal Hydrogen Electrode.

Li	− 2.96	Sb(Sb^{+++})	+ 0.1(?)
K	− 2.92	Bi	+ 0.2(?)
Na	− 2.71	As(As^{+++})	+ 0.3(?)
Ba	− 2.8(?)	Cu(Cu^{++})	+ 0.34
Ca	− 2.5(?)	Cu(Cu^{+})	+ 0.52
Mg	− 1.55	Hg(Hg^{+})	+ 0.79
Al	− 1.34	Ag	+ 0.80
Mn(Mn^{++})	− 1.0(?)	Hg(Hg^{++})	+ 0.86
Zn	− 0.76	Au(Au^{+++})	+ 1.3(?)
Cr(Cr^{+++})	− 0.5(?)	Au(Au^{+})	+ 1.5(?)
Fe$(Fe)^{++}$	− 0.44	$O_2(OH^-)$*	+ 0.41
Cd	− 0.40	I_2	+ 0.53
Ni(Ni^{++})	− 0.22	Br_2	+ 1.07
Pb(Pb^{++})	− 0.12	$O_2(H^+)$*	+ 1.23
Sn(Sn^{++})	− 0.13	Cl_2	+ 1.36
Fe(Fe^{+++})	− 0.04	F_2	+ 1.9(?)

* The potential of oxygen should, by analogy with the other elements included in the table, be that of a cell consisting of a normal hydrogen electrode and one of oxygen dipping into a solucion normal with respect to oxygen ions. But oxygen ions react with water to give hydroxide ions. Two potentials have been given in the table. The first indicated by the symbol $O_2(OH-)$ is that of an oxygen electrode dipping into a solution normal with respect to hydroxide ions, and the second (indicated by the symbol $O_2(H+)$, that of an oxygen electrode dipping into a solution normal with respect to hydrogen ions. The large difference between the two values is an expression of the fact that oxygen is a much better oxidizing agent in an acid medium than in an alkaline medium.

[1] Some authors use the opposite convention as to sign. Although their system has the advantage that positive elements are assigned positive single potentials, it causes confusion when it is used to predict which is the negative and which the positive pole in a battery. Either system is permissible since all of the values are relative; in using data of this sort care must be taken to make sure which convention is used in any particular book or article.

Since some of the elements are positive with respect to hydrogen and others are negative, it has become customary to assign to hydrogen itself the single potential zero. Since this statement merely means that no current would flow if two normal hydrogen electrodes were connected with each other, it has no particular significance, and is not used in this text. Attempts have been made to express in absolute terms the single potentials of the various elements, including hydrogen. Both the theory and the experimental results of these measurements are uncertain.

Finally, it is to be noted that when elements form more than one simple ion, the symbol of the ion contained in the solution in which the elementary electrode is dipped for making the measurement, is placed immediately after the symbol for the element in the table. Thus the difference of potential between a normal hydrogen electrode and an iron electrode is 0.43 volt when the iron dips into a normal solution of ferrous ions; the corresponding difference of potential is only 0.04 volt when the iron dips into a solution of ferric salt.[1] A question mark is placed after the more uncertain values.

Applications of the Data Concerning the Single Potentials of the Elements.—The data of the preceding table put into more precise form a number of facts qualitatively explained in earlier portions of the text. They give, for example, a better idea of the relative reducing powers of the metals and of the oxidizing powers of the non-metals, than is to be obtained from the purely qualitative table of the electromotive series in the chapter on ionization. Although the simpler table shows that the alkali and the heavier alkaline earth group metals under suitable conditions displace magnesium from solutions of its ions, the data of the potentials are required to make clear how much smaller is the tendency of magnesium to ionize. The fact that iodine and bromine in acid solution have smaller positive potentials than oxygen (see footnote to Table XXIV), while chlorine has a larger one, explains why hydriodic and hydrobromic acids are oxidized by air, and hydrochloric acid is not.

[1] This indicates that ferric ions have a greater tendency to revert to metallic iron than have ferrous ions.

In the discussion of cuprous salts (page 512), it was mentioned that only insoluble cuprous salts can be prepared by reducing cupric salts, because cuprous ions have a greater tendency than cupric ions to go over to metallic copper. The data of the table fully bear out this statement. The fact that a copper electrode, dipped into a cuprous ion solution, becomes more positive than one dipped into a cupric ion solution, means that cuprous ions reduce the electron density of the electrode more than do cupric ions, and that the former are the better oxidizing agents. Any substance, therefore, which is capable of reducing cupric ions must also reduce dissolved cuprous salts. In fact, it is possible to calculate by means of the table of potential differences, the exact equilibrium conditions in reactions of the type discussed.

The table gives general information concerning the effectiveness of the elements as reducing or as oxidizing agents. Those with large negative potentials are good reducing agents; those with large positive potentials are good oxidizing agents. The data must not, however, be used without reference to the particular reaction to which the potential applies. Gold, for example, has a very large positive potential; that is, gold ions have a strong tendency to remove electrons from the electrode with which they are in contact. Since gold itself does not take up electrons, it is evident that the large positive potential means that gold *ion*, and not metallic gold, is the substance which is a good oxidizing agent. At the same time, the large positive value of the potential means that gold itself has very little tendency to lose electrons, and is, therefore, a very poor reducing agent. On the other hand, the high positive potential of fluorine means that the free element has a very great tendency to take up electrons to form fluoride ions and is a most powerful oxidizing agent.

It must not be thought, however, that the table is a complete survey of oxidizing and reducing agents, for it contains only the elements. Similar data can be obtained for compounds. Thus a cell consisting of a normal hydrogen electrode and a platinum electrode dipping into an acidified solution of potassium permanganate, normal with respect both to permanganate and manganous ions, has a potential of about +1.52 volts. Since the positive character of the electrode is due to the removal of elec-

trons from it by permanganate, it follows that this substance is a very powerful oxidizing agent.

From the single potentials, the values of the **electromotive forces of cells** not involving the hydrogen electrode may be calculated. Thus the single potential of zinc is -0.76; that of chlorine $+1.36$. The electromotive force of the cell consisting of a zinc electrode dipping into a normal solution of zinc ions and a chlorine electrode dipping into a normal chloride solution, is the difference between the two single potentials, $1.36 - (-0.76)$ or 2.13 volts. If the Daniell cell contained normal solutions of zinc and of cupric ions its electromotive force would be the difference of the potentials of the two metals, $0.34 - (-0.76)$ or 1.10 volts. The actual cell has a saturated solution of copper sulfate and, when first set up, a solution of sodium chloride containing no zinc ions in contact with the zinc rod. Zinc ions accumulate as the cell is used, and its electromotive force is, therefore, not constant; but it nevertheless remains slightly above 1 volt. The electromotive forces of other cells are calculated in analogous fashion.

Another application of the table is in giving a precise explanation of the electrolytic separation or refining of metals. When a solution of cupric chloride is electrolyzed between a copper cathode and a platinum anode, chlorine is liberated on the platinum and copper on the copper plate. If no current from an outside source were applied, the combination would constitute a cell the electromotive force of which would be $+1.36 - (+0.34)$ or 1.02 volts. Since chlorine, in this combination, has the higher positive potential, it takes electrons away from the electrode, and copper furnishes them by sending copper ions into solution. But it is desired to cause copper ions to precipitate as metallic copper. Consequently current from an outside source must be supplied at a voltage higher than 1.02 volts. 1.02 is the approximate value of the **decomposition voltage** of cupric chloride; its actual value in any given case depends on the concentration of the solution used, and on the partial pressure of the chlorine which accumulates around the electrode. Suppose that the same calculation is now made for the voltage required to decompose a solution of zinc chloride under analogous conditions. The result is $+1.26 - (-0.76)$ or 2.12 volts. From this it follows that a current with a

voltage larger than 1.02 but smaller than 2.12 volts deposits only copper when applied to a copper and a platinum electrode immersed in a solution containing both cupric and zinc ions.

In the actual refining of copper, two copper electrodes are used, one of them consisting of the pure and the other of the impure metal; the solution employed is the sulfate of the element. Since the potential difference between the pure metal and the impure, when dipping into the same solution, is very small, a small voltage is sufficient to deposit copper on the one and to dissolve it from the other pole. This voltage is far too small to deposit zinc and other metals more active than copper, or to dissolve the less active ones.

It is now possible to explain, also, why hydrogen and not sodium is liberated when a concentrated solution of sodium chloride is electrolyzed between platinum electrodes. The presence of hydrogen at one and chlorine at the other pole would constitute a hydrogen-chlorine cell with a voltage in normal solutions of 1.36, assuming that each gas has a partial pressure of 1 atmosphere. The liberation of sodium and chlorine, on the other hand requires a voltage of $1.36 - (-2.71)$ or 4.07. Although the calculations are given for normal electrodes, the results show that under practically all conditions hydrogen must be liberated rather than sodium. It is, therefore, not logical to explain the phenomenon by assuming that sodium is liberated and that it then reacts with water to yield hydrogen.

Couples.—Two kinds of metallic coatings, which are used to protect iron from rusting, have been described in the text. In galvanized iron, the surface of the zinc, with which the iron is covered, is converted by the carbon dioxide of the air into a very closely adhering layer of basic zinc carbonate. But even when this coating is broken, the zinc affords protection. For zinc and iron, in the presence of moisture, form what is essentially a cell in which the iron is the pole to which electrons flow. Any iron which goes into solution as ions is, therefore, redeposited. Zinc, on the other hand, goes into the ionic state. The zinc ions thus formed react further with carbon dioxide giving the basic carbonate, which protects the point of rupture from further attack. Consequently, even after rupture of the protective coating, corrosion is slow, and attacks chiefly the zinc which slowly flakes off.

The other method of protecting iron is to cover it with tin (tin-plate). The covering metal is much less active than iron, and is therefore much less subject to attack by air and moisture. But once the covering is ruptured, a cell is formed in which the tin is the positive pole. Electrons therefore flow from the iron. This means that the iron goes into solution as ions. Since these ions form no adhering coating by reaction with carbon dioxide, the iron corrodes more rapidly than if no tin were in contact with it. The result is that deep holes or pits are formed. Combinations, such as those described, in which electrolytic action occurs at the point of juncture of two metals are called **couples.**

Another illustration of the action of couples is the effect of a trace of metallic copper in contact with zinc. Pure zinc acts very slowly with pure dilute sulfuric acid, because hydrogen forms bubbles on zinc with difficulty, and does not escape readily from zinc surfaces. But if the zinc is in contact with copper the action proceeds much more rapidly. In the couple formed, copper is the pole to which the electrons liberated by the ionization of zinc flow. The discharge of hydrogen ions by the electrons consequently occurs at the copper. Hydrogen gas is thus formed at a surface from which it escapes readily, instead of at zinc from which it escapes with difficulty. Platinum behaves much like copper in reactions such as that described.

Some Uses of the Hydrogen Electrode.—The electromotive force of a cell consisting of any other convenient electrode in combination with a hydrogen electrode, depends on the concentration of the hydrogen ions in the solution surrounding the latter. If all of the other factors which affect such a cell are kept constant, the concentration of hydrogen ions may be determined by measuring the actual voltage of the combination. This use of the hydrogen electrode has proved especially valuable in finding the degree of hydrolysis of salts of weak acids or of weak bases, and in determining the end point of titrations in solutions which are so highly colored that indicators cannot be employed. Many practical applications of the hydrogen electrode have been made. Its use in determining the acidity of body fluids in health and in illness has made it a valuable aid to medical diagnosis; it has been applied to the determination of the acidity of various kinds of soils,

and to the study of the effect of long continued cultivation on soil fertility; its employment in the scientific study of bacteria and moulds in media of varying acidity has led to valuable results in bread making, and in other industries involving fermentation. The actual methods and apparatus for these determinations of hydrogen ion concentration cannot, however, be understood without further knowledge of physical chemistry. Details for those interested in pursuing the subject further are given in references cited at the end of the chapter.

Dry Cells.—Cells like the Daniell cell are not very practical because of the large amount of liquid they contain. The great increase in the use of batteries of high voltage, but not required to deliver large amounts of current, has led to the development of the so-called dry cells. These usually consist of a zinc can, which serves as the negative electrode, and a carbon anode placed in the middle of the can. The space between the two electrodes is packed tightly with a moist mixture of graphite, some porous material such as crushed charcoal, manganese dioxide, zinc chloride and ammonium chloride. The zinc can be separated from the mixture by a pulpboard lining or muslin bag. The whole apparatus is sealed at the top by a layer of pitch or wax, which prevents evaporation of the water and holds the carbon electrode in place. At the negative electrode zinc ions go into solution; the liberation of hydrogen at the positive pole is prevented by the manganese dioxide, which is said to oxidize the hydrogen. The action is, however, probably somewhat more complex.

Although a single dry cell has a voltage of only 1.5 to 1.6, batteries containing a large number of the cells in series can readily be constructed. Batteries with a voltage of 45 or more are now made in very compact form. Dry cells of course suffer gradual deterioration. The electrolyte diffuses, and local action such as was described in connection with the Daniell cell occurs; at the same time loss of water cannot be entirely avoided.

Storage Batteries.—A storage battery is a device in which a chemical reaction takes place in one direction under the influence of an electrical current—that is, as a result of electrolysis with an outside source of current—and reverses itself with the liberation of electrical energy. The most widely used battery of this type is

the lead accumulator or battery. It contains two types of lead gratings, of which one is filled with finely divided lead and the other with lead dioxide. The two plates are dipped into a solution of sulfuric acid; when they are connected by a metallic conductor outside of the cell, the current flows. The source of the energy is the reduction of the quadrivalent lead in lead dioxide, and the simultaneous oxidation of metallic lead to bivalent lead ions:

$$Pb^{++++} + 2\epsilon \rightarrow Pb^{++} \quad \text{and} \quad Pb \rightarrow Pb^{++} + 2\epsilon$$

The grating containing the lead dioxide is the positive pole since the dioxide takes up electrons, and the metallic lead, which gives up electrons, is the negative pole of the battery.

In order to understand more fully the changes which take place, the other ions must also be considered. At the positive pole, the reduction of quadrivalent to bivalent lead ion leaves 2 oxygen ions, which of course at once unite with hydrogen ions of the sulfuric acid to form water. At the same time the lead ions unite with sulfate ion to form insoluble lead sulfate which is deposited in the grating. The reaction may be written:

$$PbO_2 + 2\epsilon + 2H_2SO_4 \rightarrow PbSO_4 + 2H_2O + SO_4^{=}$$

What happens to the excess of sulfate ions will become clear when the changes at the negative pole are considered. There lead is being converted into lead ions; these unite with sulfate ions of the acid to form lead sulfate which is thus deposited on this pole also:

$$Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2\epsilon$$

Sulfate ions in excess are liberated at the positive and hydrogen ions at the negative pole. It is clear that they will intermingle by diffusion, and, since they are present in just the right proportion, will constitute sulfuric acid. At both poles sulfuric acid is used up. Consequently the solution in the battery becomes continuously weaker as the cells deliver current. The strength of the acid is conveniently determined by measuring its density with a hydrometer; this device is usually used to determine how nearly exhausted the battery is.

When necessary, the cell may be recharged by reversing the current which the cell delivers. This results in the reverse of the reactions which occur when the cell acts as a source of current. At the positive pole the following reaction occurs:

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + H_2SO_4 + 2H^+ + 2\epsilon$$ [1]

At the other electrode, lead sulfate is reduced to metallic lead, and sulfate ions are set free. At the positive pole there is an excess of hydrogen ions, at the negative pole an excess of sulfate ions, and these intermingle by diffusion to constitute sulfuric acid. The concentration of the acid therefore increases during charging of the battery; the process may be followed by the use of a hydrometer to determine when the acid has reached the density characteristic of a fully charged battery.

The lead storage battery possesses many advantages. In the first place lead sulfate, the product of both oxidation and reduction, is insoluble and adheres to the plates; this makes possible the electrolytic reversal of the reaction which produces current. In the second place, because hydrogen ions diffuse rapidly the current is readily carried from one plate to the other within the battery—in other words, the internal resistance of the battery is relatively small. The energy changes attending the various reversible reactions involved in charging and discharging the battery are high, and on this account, a large quantity of energy may be "stored." The disadvantages are the great weight of storage batteries made of lead, and the necessity of using a corrosive liquid in them.

The **Edison Storage Battery** consists of one iron plate and a second plate which contains nickelic oxide, Ni_2O_3, when the cell is charged; potassium hydroxide solution is the electrolyte. The reversible reaction of the cell is:

$$Fe + 3H_2O + Ni_2O_3 \rightleftarrows Fe(OH)_2 + 2Ni(OH)_2$$

The battery is lighter than the lead cell, is not readily injured by overcharging or by standing uncharged, and makes use of a

[1] The quadrivalent lead ions may in part unite momentarily with sulfate ions to form $Pb(SO_4)_2$. This salt is, however, completely hydrolyzed to lead dioxide and sulfuric acid.

somewhat less objectionable electrolyte. Its internal resistance is higher than that of the lead cell. For this reason it delivers current less rapidly, and is therefore not so well suited for such purposes as starting automobile engines for which current is needed in large amounts for short periods of time.

EXERCISES

(1) (*a*) What type of chemical reactions may be utilized in cells for the production of electrical current? (*b*) Give an illustration of such a reaction (other than those discussed in the text), and describe a device in which it might be carried out so as to deliver current.

(2) (*a*) Upon what does the amount of current delivered by a cell depend? (*b*) Upon what does the voltage of the cell depend?

(3) (*a*) Explain what happens when a piece of metal is dipped into water. (Assume that the metal is one which does not react readily with water.) (*b*) Explain why, when a metal like zinc which has a great tendency to ionize, is dipped into water, only a minute portion of it actually forms ions. (*c*) Explain why the difference of potential between a metal and a solution of its ions depends on the concentration of the latter.

(4) In the electromotive series, as used in this text, why do the most electropositive elements exhibit the largest negative single potentials?

(5) (*a*) What would be the electromotive force developed by a cell consisting of a lead electrode dipping into a normal solution of lead ions and a mercury electrode in contact with a normal solution of mercurous ions? (*b*) Would the potential difference be increased or decreased by using a tenth normal solution of lead ions in place of the normal solution? (*c*) What would be the effect of decreasing the concentration of mercurous ions?

(6) (*a*) What would be the difference of potential between a normal hydrogen electrode and a mercury electrode in contact with a normal solution of mercurous ions? (*b*) How would the addition of sodium hydroxide to the solution around the hydrogen electrode affect the potential difference? (Note:—In answering part "*b*" of this question bear in mind the following points. Although the arbitrary value, 0.0 is assigned to the single potential of hydrogen, this does not mean that no ionization of hydrogen occurs. It merely means that hydrogen in equilibrium with its ions is less positive than lead, for example, and more positive than antimony. When sodium hydroxide is added, hydrogen ions in the solution will be used up and the potential of the

electrode will change. The nature of the change may be determined by considering whether the decrease in the concentration of hydrogen ions in solution causes more hydrogen to ionize or more hydrogen ions to form hydrogen. When this point is decided, consider whether the result causes the hydrogen electrode to become more or less negative than it originally was.)

(7) Explain why, in setting up a cell, it is necessary not only to connect the two metals by a metallic conductor but also to connect the two solutions by a conducting liquid.

(8) (*a*) Describe the Daniell cell, and explain why it operates satisfactorily. (*b*) Write the chemical equations for the reactions taking place during its operation and calculate how much zinc would be used if the cell were to deliver 10,000 coulombs.

(9) (*a*) Explain why the addition of a trace of copper sulfate to sulfuric acid increases the rate of reaction of the acid with zinc. (*b*) Why must only a trace of copper sulfate be used? (Consider the mechanical effect of the deposit formed if much copper sulfate is used.)

(10) Explain the operation of the lead storage battery, writing the reactions which take place at each electrode during charging and during delivery of current.

(11) (*a*) Explain why the lead storage battery is so successful. (*b*) Mention some of its disadvantages.

REFERENCES

In place of collateral reading the student is advised to review electrochemical processes in the light of this chapter. See for example chlorine, hypochlorites, chlorates, sodium and sodium hydroxide.

CHAPTER XXXIX

CHROMIUM AND THE LESS COMMON ELEMENTS OF THE FIFTH AND SIXTH SUB-GROUPS

Werner's Theory

Chromium is the only element of the fifth and sixth sub-groups usually taken up in courses of general chemistry. Of the others, **columbium** [1] and those elements which are products of radioactive decompositions are rare. Vanadium, molybdenum, and tungsten [1] are moderately abundant and have found important uses. **Vanadium** is added to steel to make it harder and to increase its tensile strength; **tungsten** is used for similar purposes. Tools made of tungsten steel are particularly useful because they do not readily lose their hardness at moderately high temperatures, as do those made of ordinary steel. Lathes may, therefore, be operated at much higher speeds with tools made of the tungsten alloy. Its use thus greatly reduces the time and labor required for the large scale manufacture of certain articles. Tungsten, because of its high melting point and low vapor pressure, is extensively used for filaments of incandescent electric lamps. If the bulb containing the filament is filled with nitrogen, the gradual evaporation of the metallic tungsten is further decreased, because the presence of the nitrogen molecules decreases the rate of diffusion of the small amount of tungsten vapor. As originally obtained, the metal is in the form of a powder the melting point of which is so high (3350°) that attempts to make wires of it by a process of melting are impracticable. But when the powder is

[1] In certain European countries, tungsten is called wolfram. The latter name is the origin of the symbol Wo universally used for the element. Columbium is sometimes called niobium. Note that in the description of the rarer elements of these groups, the periodic arrangement is not adhered to in the text.

very hot, though not yet melted, it may be compressed into brittle bars. These are then heated at 1500° in an atmosphere of hydrogen. By gradually drawing out the resulting material, and by heating it repeatedly a very malleable and tenacious form of the metal is finally obtained. Tungsten is now also used to replace platinum in contact points, for it is not readily oxidized by air, and is not attacked by the ordinary acids. **Tantalum** was at one time used in incandescent lamps, but it has been displaced by tungsten; its commercial possibilities have, however, not been fully developed. **Molybdenum** has been used to replace tungsten in high speed tools; in this respect it has not so far proved satisfactory because its action is uncertain. It is added in small amounts, together with chromium, to increase the tensile strength of steel which is to be used for crankshafts and axles. These special steels represent one of the developments of chemistry which has made the modern automobile possible. **Uranium** is not very extensively used; its chief interest is its relationship to radium which has already been discussed.

In spite of the important uses and relations of these elements they are not to be discussed in detail because of the complexity of their reactions and compounds. Thus vanadium, tungsten and uranium are known to form four chlorides each; molybdenum has at least six oxides. Most of the compounds, however, are even more complex, and their structure is as yet little understood.

Chromium

Chromium is found quite abundantly as the ore, chromite, $Fe(CrO_2)_2$. The metal is obtained in the form of an iron alloy, ferrochrome, by reducing the ore with carbon in electric furnaces. Ferrochrome is used to make alloys of steel and chromium which are characterized by great strength. Other alloys of chromium are used in stainless cutlery because, when the content of chromium is fairly high, the alloys are very slightly affected even by boiling acids. Three-fourths of the special steels made in the United States are said to contain chromium. The pure free metal is made by the Goldschmidt process (reduction with aluminium), but it is expensive and is not much used. Alloys of nickel and

chromium, known commercially as "nichrome," are employed because of their high melting points in the resistance elements of electric furnaces, and in "thermocouples."[1] Metallic chromium is hard and brittle; it burns in oxygen, is readily attacked by the halogens, hydrochloric and sulfuric acids, but curiously, not by cold nitric acid, in which the metal becomes passive. (See page 503.)

Chromium is bivalent positive in **chromous** compounds such as chromous chloride, $CrCl_2$, trivalent in **chromic** compounds, such as chromic chloride, $CrCl_3$, and has a valence number of six positive in **chromates** and **dichromates.** Because of these relations, chromates and dichromates are capable of acting as moderately strong oxidizing agents. In the course of such reactions, they are always reduced to chromic salts; their behavior in this respect has already been sufficiently discussed. (See pages 148, 278, 279 and 283.) Chromic salts may, of course, be oxidized to chromates. Potassium permanganate in acid solution may be used to effect the oxidation, but the reaction is usually carried out in an alkaline medium. The method is illustrated in the preparation of chromates (page 575).

Although it is not difficult to oxidize chromic salts, they are not used as reducing agents because the reaction does not proceed with sufficient readiness. Since chromium forms compounds in which its valence is two positive, the trivalent positive chromic ions might conceivably act also as oxidizing agents. But the tendency for chromic salts to go over into chromous salts is very slight. Chromous salts, on the other hand, are oxidized with the utmost ease to chromic compounds. Exposure of an aqueous solution of a chromous salt to the air for a few seconds is sufficient to effect the oxidation; in the absence of air, the chromous salt reduces the hydrogen ion of the water present, liberating hydrogen, and becoming oxidized to the chromic salt.

For the reasons given **chromous salts** are not frequently encountered in chemical work. It is interesting to note that most of the anhydrous chromous salts are white, and that the hydrated forms are highly colored. Most of the latter are intensely blue;

[1] Thermocouples are devices for measuring temperature; they are extensively used when the temperatures to be determined are high.

the acetate, which because of its insolubility is the easiest chromous salt to prepare and keep, is red; the hydroxide is yellow.

Chromic salts are usually obtained by the reduction of chromates, for example with zinc and hydrochloric acid. The resulting solution of chromic chloride may be treated with sodium or ammonium hydroxide to precipitate chromic hydroxide, and from the latter other chromium salts may be prepared by the action of the corresponding acids. **Chromic ion** resembles aluminium ion in many respects. Thus chromium hydroxide is a very weak base. All of its salts are somewhat hydrolyzed; the reaction is complete with the carbonate and sulfide as with the corresponding aluminium salts. The hydroxide, like aluminium hydroxide, also possesses feeble acid properties. For this reason it dissolves in bases to form the green **chromites**:

$$Cr(OH)_3 + NaOH \rightarrow \underset{\text{sodium chromite}}{NaCrO_2} + 2H_2O$$

Further points of resemblance between chromic and aluminium salts are their solubility and stability relations. The nitrates, halides and sulfates of both are soluble in water; most of the other common inorganic salts are insoluble. Salts like the sulfates are decomposed at moderately high temperatures into the oxides; the hydroxides much more easily. Chromic oxide, like aluminium oxide, if formed at high temperatures, is very insoluble, but if obtained at moderately low temperatures, it has a much greater solubility. Chromic sulfate forms chrome-alums with sulfates of the alkali metals. These double salts are in all respects analogous to the corresponding aluminium compounds. Chromic ion differs from aluminium ion as follows: (1) it may be oxidized to chromate ion or reduced to chromous ion, (2) it has a great tendency to enter into complex ions, and (3) its compounds display a great variety of colors.

The colors of the chromium compounds are so striking that the element owes its name to this phenomenon. The colors of chromous salts have already been mentioned; chromates are yellow, and dichromates orange. Chromic salts exhibit an even greater variety of colors as may be illustrated in the case of the chloride. The anhydrous substance, prepared by treating the metal with

chlorine at high temperature, is of a beautiful dark violet shade. It is insoluble in water, but may be caused to dissolve by adding a minute fragment of chromium to the mixture of the salt and water. This solution is also violet, but of an entirely different shade from that of the anhydrous material. When boiled the solution turns green. These color changes are due to the formation of complex hydrates which will be discussed briefly in the following paragraphs.

Complex Compounds of Trivalent Chromium.—When anhydrous chromium chloride is treated with liquid ammonia, two compounds are formed. One of these is canary yellow and the other bright red; the first has the formula $CrCl_3 \cdot 6NH_3$; and the second, $CrCl_3 \cdot 5NH_3$. By removal of ammonia from these compounds it is possible to prepare others corresponding to the formulae $CrCl_3 \cdot 4NH_3$ and $CrCl_3 \cdot 3NH_3$, each of which possesses a characteristic color. In addition to the differences in colors, these compounds are distinguished by very decided differences in chemical behavior. The first substance, $CrCl_3 \cdot 6NH_3$, when dissolved in water yields 4 ions as shown by freezing point lowering. Silver nitrate added to a solution of 1 gram molecular weight of the salt precipitates 3 gram molecular weights of silver chloride, thus demonstrating that three of the ions are chloride ions. On the other hand, the solution displays none of the properties characteristic of ammonia; it has no odor, is neutral in reaction and does not give off ammonia when boiled. These facts lead to the conclusion that the 6 molecules of ammonia and the chromic ion are united to form a complex ion. All of this may be indicated by writing the formula of the salt $[Cr(NH_3)_6]^{+++}Cl_3^-$.

The second compound yields but 3 ions, 2 of which may be shown by precipitation with silver nitrate to be chloride ions. The ammonia, one of the chlorine atoms and the chromium constitute the complex ion. These facts may likewise be indicated in the formula $[Cr(NH_3)_5Cl]^{++}Cl_2^-$. In the same way the behavior of the third salt is described by the formula $[Cr(NH_3)_4Cl_2]^+Cl^-$. The last compound is a non-conductor and therefore not ionized, as is shown by the formula $[Cr(NH_3)_3Cl_3]$.

These formulae for the complex positive ions reveal the striking fact that in addition to the chromium atom, or ion, each complex ion contains 6 other ions or molecules. The tendency of the chromium to surround itself by six other groups or ions is further shown by the following experiment. It is impossible to remove the remaining 3 molecules of ammonia from the compound, $Cr(NH_3)_3Cl_3$, by heating the substance

in an atmosphere of hydrogen chloride; the hydrogen chloride instead of removing the ammonia, adds on to the compound, and forms the new substance $(NH_4)_3{}^+[CrCl_6]^{=}$. In the latter the chromium is in the negative ion, because the 6 chloride ions more than neutralize the three positive charges of chromic ion; but the striking part of the phenomenon is that here again the chromium is associated in the complex ion with six other groups. The same sort of relationships are observed in the hydrated chromium salts. Thus the violet hydrated chromium chloride, mentioned in a preceding section of this chapter, has 6 molecules of water and yields 4 ions; its formula may be written $[Cr(H_2O)_6]^{+++}Cl_3^-$ to indicate these facts. The green hydrated chloride which has only 4 molecules of water, yields only 2 ions, and its formula is, therefore, written $[Cr(H_3O)_4Cl_2]^+Cl^-$.

Although the reappearance of the number six in the grouping of ions and molecules about the chromium ion is in itself striking, it is rendered even more important by the fact that this same phenomenon is exhibited by hundreds of complex chromium compounds, and by an even greater number of complex compounds of cobalt, of iron, of iridium, of platinum, and of many other elements. Evidently a phenomenon of such frequent occurrence must be due to some fundamental cause of general significance. It is impossible, however, to discuss this matter in detail, and the following outline of the theory developed by Werner to account for the facts described is very incomplete.

According to **Werner's theory** (restated in somewhat modified terms), a highly polar compound such as chromium chloride creates an electromagnetic field which attracts other polar groups or compounds. These arrange themselves about one or the other of the ions of the original substance in such a way as to form a stable spacial arrangement. The most symmetrical of these arrangements are the octrahedron and the tetrahedron. An octahedron has eight faces and six corners, a tetrahedron four faces and four corners. The atom or ion which forms the complex is considered to occupy the center of one of these figures, and is therefore called the "central atom." If the atoms grouped about the central atom occupy the corners of these imaginary octahedra or tetrahedra, the complex ion should contain either six or four groups (see Fig. 29). The frequent appearance of six added groups in the complex ions has already been pointed out; in many other compounds, however, four added groups are found in the complex ions so that Werner's theory has been amply corroborated in this respect. Since in a compound like $[Cr(NH_3)_6]Cl_3$, the chromium and the six ammonia molecules are held together, they are said to be co-ordinate, or held in the co-ordination sphere; the number six or four which designates the number of groups so

held by the central atom is called the **co-ordination number** of the compound (or central atom); and the theory is often called the **co-ordination theory.**

By some chemists, Werner's theory is considered an important extension of the theory of ionization. According to this point of view, no salt separates into free ions without first "completing" the co-ordination sphere, that is, without first taking on six, or four, groups to surround one of the simple ions. When a salt like sodium chloride dissolves in water, it is assumed first to become hydrated, and then to yield electrolytic ions. In molten salts, complexes such as $[NaCl_6]^{5-}$, are postulated. Because

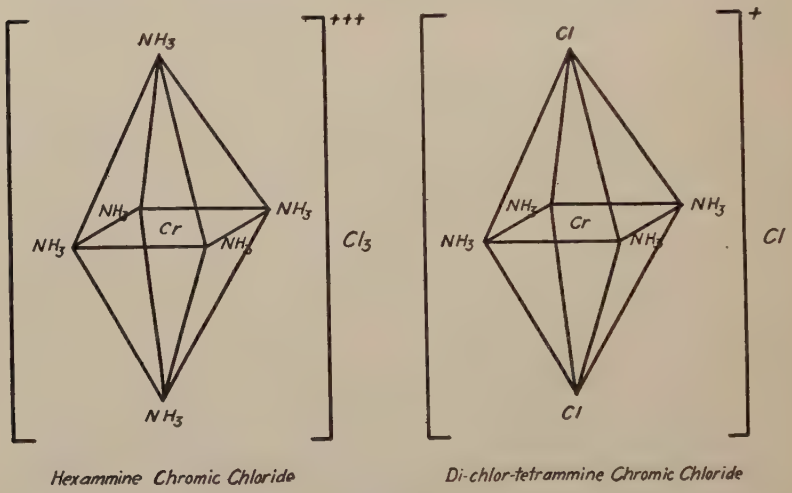


Fig. 29.

of the great instability of these hypothetical ions, it is difficult to prove or disprove their existence. Although these assumptions are attractive for many reasons, no evidence of decisive value has as yet been adduced in their favor. Nevertheless application of the co-ordination theory to the very complex compounds of silicon, molybdenum, tungsten, etc., has been very successful. This application is still in its infancy, but the probability that it will ultimately displace the older views seems so great that the older explanations have been omitted in this text.

The theory has led to a vast amount of experimental work, and has been particularly noteworthy for its success in predicting isomers which were not known until attempts to verify the theory led to a search for them. In practically all instances the expected results were realized. Never-

theless the theory in its present form is probably only a partial statement of the fundamental truth, since there are a number of important facts for which it does not furnish an adequate explanation. It is not unlikely that, after more is known about the structure of the heavier, inner group elements which most readily form these stable complex ions, the rather indefinite forces postulated by Werner as holding the groups in the co-ordination sphere will be explained in terms of electron sharing.

Preparation of Chromates.—Chromates are prepared by roasting a mixture of the mineral chromite, $Fe(CrO_2)_2$, and potassium carbonate in contact with air. Lime is usually added to keep the mass porous so that oxygen may have access to all of the material. The reaction is:

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2$$

If lime is used, some of the chromate will be in the form of the calcium salt, which is transformed to potassium chromate by the addition of potassium sulfate before the mixture is extracted with water. When chromates are prepared on the small scale, it is convenient to hasten the reaction by adding an oxidizing agent, such as potassium chlorate, to the mixture of chromic salt and potassium carbonate. Chromates are also obtained when chromic hydroxide, suspended in water, is boiled with a solution of sodium peroxide:

$$2Cr(OH)_3 + 3Na_2O_2 \rightarrow 2Na_2CrO_4 + 2NaOH + 2H_2O$$

The last reaction is often used to separate chromic ion from other ions, and to identify it in qualitative analysis.

Properties of Chromates and Dichromates.—The importance of chromates as oxidizing agents has already been discussed. (Pages 278–283.) Insoluble chromates find application in the manufacture of pigments for paints because of their intense yellow color. Most of the chromates, except those of the alkali metals and of magnesium are but slightly soluble in water; the chromates of the other alkaline earths and of lead are so insoluble that these ions are precipitated as chromates in qualitative analysis, for purposes of separation and identification.

When a solution of a chromate is treated with an acid, the yellow color of the solution turns to a reddish orange. The addi-

tion of an acid to chromates should produce the acid chromates, because the second hydrogen ion of chromic acid is much less dissociated than the first. This reaction, if it occurred, would be represented by the equation:

$$2K_2CrO_4 + 2H_2SO_4 \rightleftarrows 2KHCrO_4 + K_2SO_4$$

But the solution does not contain the substance $KHCrO_4$. Instead, potassium dichromate, $K_2Cr_2O_7$, is formed. Apparently the two acid chromate ions have lost 1 molecule of water:

$$2HCrO_4^- \rightleftarrows Cr_2O_7^= + H_2O$$

The whole set of reactions in ionic form is:

$$2CrO_4^= + 2H^+ \rightleftarrows 2HCrO_4^- \rightleftarrows Cr_2O_7^= + H_2O$$

Since all of the reactions are reversible, addition of a base, which removes hydrogen ion, should reconvert the dichromate ion into chromate ion; as a matter of fact, a base changes the orange color of a dichromate to the yellow color of the chromate. The reversibility of the reaction also shows that a solution of a chromate must possess all the properties of that of a dichromate, in addition to its own, and *vice versa*. For this reason no special properties can be assigned to either ion; dichromates and chromates behave in solution as if they had the same properties. Dichromates are, however, in general more soluble in water than chromates.

Free chromic acid is unknown. When concentrated sulfuric acid, which might be expected to liberate chromic acid, is added to chromates or dichromates, **chromic anhydride,** CrO_3, is precipitated in red needles. When this substance is dissolved in water, a solution of chromic acid is obtained:

$$CrO_3 + H_2O \rightleftarrows H_2CrO_4$$ [1]

An interesting reaction occurs if solutions of chromates or dichromates, acidified with dilute sulfuric acid, are treated with hydrogen peroxide. If the solution is not too acid, a beautiful blue

[1] Probably the reaction is not complete, and some chromic anhydride dissolves as such. Dichromic acid is also probably formed ($2CrO_3 + H_2O \rightleftarrows H_2Cr_2O_7$), as well as other more complex acids such as $H_2Cr_3O_{10}$ and $H_2Cr_4O_{13}$.

color appears. This color is due to a substance which is soluble in ether, and the color is more easily seen if the reaction mixture is shaken with ether, because the blue material is then extracted from the solution colored by the other chromium compounds. The nature of the blue substance is still in dispute; its formula is written $HCrO_5$ by some authors, and H_3CrO_8 by others. It seems to be a peroxide of chromic acid, somewhat analogous to persulfuric acid (see page 270). The production of the blue color is used as a very sensitive test for chromates or for hydrogen peroxide.

EXERCISES

(1) (*a*) What are the advantages of tungsten for use in filaments of incandescent lamps? (*b*) What is the advantage of the nitrogen-filled bulbs?

(2) (*a*) Explain why chromous compounds are seldom encountered in chemical work. (*b*) Why is chromous acetate the easiest chromous salt to prepare?

(3) Write the equation for the reduction of potassium dichromate to chromic chloride by zinc in hydrochloric acid solution. Use the electronic method for balancing the equation.

(4) (*a*) In what respects are chromic salts similar to those of aluminium? (*b*) In what respects do they differ?

(5) (*a*) Explain why chromium hydroxide dissolves in hydrochloric acid. (*b*) Why is chromium hydroxide precipitated when a solution of chromium sulfate is treated with sodium carbonate? (See pages 535 and 571.)

(6) Explain why chromium hydroxide dissolves in sodium hydroxide?

(7) (*a*) Write the equation for the preparation of potassium chromate. (*b*) Explain why, if calcium chromate is obtained in the reaction as a result of the use of lime in the original mixture, potassium carbonate is used to transform the calcium salt into potassium chromate.

(8) (*a*) What sort of salt is potassium dichromate? (In answering, consider from what unstable ion it is probably derived.) (*b*) Explain why the addition of an acid converts the chromate ion into the dichromate ion and why bases cause the reverse reaction. Write equations to represent the equilibria involved.

(9) Explain why the addition of a barium salt, such as barium nitrate, to an aqueous solution of potassium dichromate causes the precipitation of barium chromate. Write equations to indicate the

equilibria involved. In answering, consider the fact that barium chromate is very slightly and barium dichromate very soluble in water.

(10) Name two reducing agents which are easily oxidized by chromates in acid solutions. Write the equations for the reactions chosen and balance them by the electronic method.

REFERENCES

H. Wysor—Metallurgy (1914). For the metallurgy of the group. An excellent introduction to Werner's Theory.

Schwarz—The Chemistry of the Inorganic Complex Compounds. (Translated by L. W. Bass.) (1923.)

General References in Chapter XXXII of this text.

CHAPTER XL

MANGANESE

Comparison of Main and Sub-groups

Manganese is the only member of the seventh sub-group yet discovered. It is found in nature chiefly as pyrolusite, MnO_2, the largest deposits of which are in Russia and in Brazil. To obtain the pure metal from the ore, the Goldschmidt aluminothermic process is used. In industry the metal is employed chiefly in the form of alloys with iron. An alloy containing less than 20 per cent of manganese is called spiegeleisen; alloys richer in manganese are known as ferromanganese. By adding these alloys to steel in the proper proportion the hardness of the latter is greatly increased. An alloy of manganese (12 per cent), copper (84 per cent), and nickel (4 per cent) is known as manganin; it is used in making resistance units for electrical apparatus, because its resistance changes very little with small changes in temperature.

The element is a fairly brittle metal; it is oxidized superficially by air; it reacts readily with the electronegative elements such as the halogens, and liberates hydrogen from dilute hydrochloric and sulfuric acids; it is an active reducing agent. In other words, it is a fairly electropositive element, as shown also by its position in the electromotive series. The valence or valence numbers of manganese in its various types of compounds are as follows: in manganous compounds two, in manganic compounds three, in manganese dioxide and manganites four, in manganates six, and in manganese heptoxide and permangangates seven positive. Each of these types of manganese compounds possesses not only specific chemical properties, but characteristic colors as well. Thus manganous salts are almost white when anhydrous, and pink when hydrated; manganic salts are purple, somewhat like permanganates; manganese dioxide and other compounds in which man-

ganese is tetravalent are usually brown or black; manganates are deep green in solution, although dark violet when solid and free from water; permanganates are black with a violet cast in the solid state, and deep purple when in solution.

The chemical differences between the various types of manganese compounds are of the kind already described in the cases of other elements which exist in compounds of various valence stages. Thus manganous hydroxide ($Mn(OH)_2$) is a moderately strong base, and its salts are not very extensively hydrolyzed. Manganic hydroxide ($Mn(OH)_3$) is a very weak base; its salts are more extensively hydrolyzed than those of bivalent manganese. Manganese dioxide is the anhydride of an hydroxide which must be both an extremely weak base and an extremely weak acid, because it forms salts such as manganese tetra-acetate, $Mn(C_2H_3O_2)_4$, and manganites, such as calcium manganite, $CaMnO_3$, both of which are almost completely hydrolyzed by water. Manganates are derivatives of a moderately weak acid, H_2MnO_4; permanganic acid ($HMnO_4$) is, on the other hand, one of the strongest of all acids. This series of compounds again illustrates the fact that with increasing positive valence of a given element, the hydroxides become less basic and more acidic.

Another relationship, to be anticipated from the behavior of other elements, is that the manganous compounds are moderately good reducing agents, and permanganates strong oxidizing agents. Thus the former are oxidized to compounds of trivalent manganese or to manganese dioxide by chlorine or bromine, by nitric acid, and by permanganates, to cite but a few illustrations. In general, oxidation of manganous compounds proceeds best in an alkaline medium. When manganous hydroxide is precipitated by an excess of sodium hydroxide, the fresh hydroxide is quite rapidly oxidized even by the air to a compound of trivalent manganese, MnO(OH). Permanganates, on the other hand, are most completely reduced in acid solution in which they are converted by all reducing agents to manganous salts. In alkaline solution, however, they are reduced only to manganese dioxide. This is to be expected, for in such solutions permanganates oxidize manganous compounds to manganese dioxide, as illustrated in the equation:

$$2KMnO_4 + 3Mn(OH)_2 \rightarrow 5MnO_2 + 2KOH + 2H_2O$$

All manganese compounds are prepared directly or indirectly from manganese dioxide (pyrolusite). **Manganous salts** are, of course, obtained by reduction of this compound. The action of hydrochloric acid on the dioxide, for example, yields chlorine and manganous chloride. The latter may be obtained from the solution in crystallized form by evaporating the filtered liquid to dryness. Before this is done, iron present as an impurity is removed by precipitation as the hydroxide. This separation may be carried out without much difficulty, since the hydroxides of iron are less soluble than those of manganese, and are, therefore, precipitated before manganous hydroxide when a base is carefully added. From the purified manganous chloride, the corresponding hydroxide may be precipitated, and from the latter other manganous salts may be prepared. With the exception of the halides, the sulfate, and the nitrate, most of the inorganic manganous salts are but slightly soluble.

Manganic salts and compounds in which the valence number of the manganese is four are, with the exception of the dioxide, not very stable, nor of any practical importance.

Potassium manganate is prepared by fusing manganese dioxide with potassium hydroxide in the presence of air:

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

In order to make the reaction go to completion the mixture must be heated in a rotary kiln in which it is continuously pulverized. As this is difficult to do on the small scale, an oxidizing agent such as potassium chlorate is usually added when the material is prepared in the laboratory. As long as an excess of potassium hydroxide is left or any moisture is present, the mass has a green shade; upon the completion of the reaction, if excess of hydroxide is avoided, the material is dark violet in color. When it is dissolved in water, however, the deep green color reappears.

Pure potassium manganate cannot be obtained by this method. The pure salt is most easily prepared by heating potassium permanganate with a very concentrated solution of potassium hydroxide:

$$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + O_2 + 2H_2O$$

The manganate is not soluble in the concentrated hydroxide, which is present in excess, and may be separated from it by filtration. Sodium manganate cannot be prepared in this way with any degree of purity because it is very soluble; in fact, no manganate except that of potassium has been prepared in a pure state.

Manganates, in themselves, are not of great importance. They are very unstable; they break down readily into manganese dioxide and oxygen, and are decomposed by water. They are formed, however, as an intermediate step in the manufacture of **permanganates.** Manganese dioxide is fused with potassium hydroxide in the presence of air as described above. The cooled melt is then extracted with a dilute solution of potassium hydroxide, yielding a solution of potassium manganate. From this, the permanganate may be obtained in a variety of ways. The simplest is to treat the solution with carbon dioxide. The chemical change involved in this method is made clear by considering the reaction which occurs when manganates are dissolved in water:

$$3K_2MnO_4 + 2H_2O \rightleftarrows 2KMnO_4 + MnO_2 + 4KOH$$

The addition of carbon dioxide neutralizes the potassium hydroxide and, therefore, drives the reaction to the right. The resulting solution contains both potassium permanganate and the corresponding carbonate; of these salts the former, which is the less soluble, crystallizes out when the solution is concentrated. Sulfuric acid might, or course, be used instead of carbon dioxide; but the latter is cheaper, and potassium permanganate is more readily separated from the carbonate than from the sulfate. Potassium manganate may be transformed into permanganate by electrolytic oxidation instead of by chemical means. The electrical method has the advantage that it converts almost all of the manganate into permanganate, whereas in the process described above one-third of the manganate goes to manganese dioxide. Permanganates are also prepared by direct oxidation of metallic manganese by the electric current; this method has lately come into considerable use.

Summary of the Most Important Properties of Permanganates. —Since permanganic acid is very highly ionized, its salts are in general only slightly or not at all hydrolyzed. All permanganates

are powerful oxidizing agents; the differences between their reactions in dilute acid and in dilute alkaline solutions have already been discussed (page 580). In strongly alkaline solutions permanganates decompose spontaneously into manganates with evolution of oxygen as illustrated in the method for making pure potassium manganate; addition of concentrated sulfuric acid, on the other hand, liberates the volatile, extraordinarily explosive manganese heptoxide, Mn_2O_7. When heated, permanganates are decomposed, sometimes explosively, probably into manganites, such as K_2MnO_3, and oxygen.

Brief Comparison of Main and Sub-groups of the Periodic System.—Chromium and manganese are in no important respects similar to the elements of the corresponding sixth or seventh groups of the outer series. It is true that chromium, sulfur, selenium and tellurium exhibit a maximum positive valence number of six, and that manganese, chlorine, and iodine form compounds in which the valence number is seven positive. But these are the only grounds for classifying chromium and the elements of its group as a sub-group of the sulfur family, and for considering manganese as a member of a hypothetical group analogous to the halogens in the outer series. The differences in properties are far more marked than these purely formal similarities. Chromium is a metal and, as such, forms positive ions in solution; it exhibits the valences two and three positive in addition to the valence number six, and is never negative. The members of the sulfur family, on the other hand, are non-metallic; they do not exist as free positive ions in solution, but do form ions in which their valence is two negative; their positive valence numbers are four and six but not two, three and six as in the case of chromium. Similar differences between manganese and the halogens might be pointed out.

Although the difference between the elements of the main and sub-groups in the sixth and seventh columns is very marked, it is not an exceptional case. The members of the alkali metal group and those of the copper group, which constitute the first main and sub-groups respectively, are, to be sure, all metals; but no other similarity exists between them except that all members of both groups form univalent positive ions. The alkali metals are

the most electropositive of all elements; they form no stable complex ions; they exhibit only a single valence; their hydroxides are the strongest bases; and the group is very uniform. The elements of the copper group are among the least electropositive metals; their hydroxides are not strong bases; the ions form a great variety of stable complexes; two of the elements exhibit more than one valence; and the group in many respects lacks the great uniformity characteristic of the families of the outer series. Similar contrasts are found between the alkaline earth group and the zinc group. As a matter of fact, it is only in the fourth group of the periodic system that main and sub-group have any close relationship to each other. It must be concluded, therefore, that the classification into main and sub-groups is a somewhat artificial one. It is justified because it simplifies the representation of the periodic system by means of tables, and because contrasts, like similarities, are of value in organizing great numbers of facts. Whether any theoretical relationship between sub-groups and main groups exists is not known at present; a satisfactory theory of the structure of the atoms of the sub-groups would answer this question, but such a theory has not as yet been developed.

EXERCISES

(1) What experimental facts support the statement that manganese is a fairly electropositive metal?

(2) (*a*) Illustrate with various manganese compounds the rule that when an element forms compounds in which it has different valences, the strength of the hydroxides as bases decreases, and their strength as acids increases with increase in positive valence. (*b*) Cite as many other illustrations of the rule as you can.

(3) (*a*) Name two reducing agents which are readily oxidized by chromates in acid solutions. Write the equations for the reactions chosen and balance them by the electronic method. (*b*) Answer as in (*a*) but for potassium permanganate.

(4) (*a*) Suggest a method of preparing manganous sulfate from manganese dioxide. Write the equations for all the reactions involved. (*b*) Answer as in (*a*) but for the preparation of potassium permanganate from manganese dioxide.

(5) Write the equation for the reaction which occurs when manganese dioxide is converted into potassium manganate by fusion with potassium

hydroxide and potassium chlorate. Assume that the chlorate acts as the sole oxidizing agent and that, in the course of the reaction, the chlorate is reduced to the chloride. Use the electronic method of balancing the equation.

(6) Why is it more difficult to prepare sodium manganate than the corresponding potassium salt?

(7) Name the most important chemical properties of permanganates, and illustrate each by an equation.

REFERENCES

See Chapter XXXII.

CHAPTER XLI

THE EIGHTH GROUP OF THE PERIODIC SYSTEM

The Iron Group.—The Platinum Metals

By analogy with the outer series of the periodic system, a group of zero valence should follow the seventh sub-group, the sole representative of which is manganese. Instead of such a group, however, each of the inner series has a sequence of three elements in the place where this zero group ought to be. These elements are quite similar to each other but do not have zero valence. Thus manganese is followed by iron, cobalt, and nickel.[1] If the system used in constructing the other parts of the table were to be used here, each of these three elements would be the first member of a separate group. The most consistent properties of the periodic system, however, are the characteristic valence of each group and the change in valence from group to group in steps of one. But iron, cobalt and nickel all exhibit the same valences, two and three positive. The three elements are, therefore, assigned to what really is a single place in the table. There is another reason for not making three separate groups. If this were done, iron, ruthenium and osmium would constitute the first, cobalt, rhodium and iridium the second, and nickel, palladium and platinum the third of the three groups. But iron is, in most respects, more closely allied chemically to cobalt and nickel than to ruthenium and osmium, iridium is in many ways more like platinum than like cobalt, and so on. All of these relationships are brought out more clearly than could be done with the scheme

[1] According to their atomic weights, the elements should be placed in the order iron, nickel and cobalt. Both chemical properties and atomic numbers show that the order given in the text is the correct one. The case is another illustration of the displacement of elements from their proper positions because of the existence of isotopes. (See page 369.)

followed in other groups by making an unusual sort of place for these elements in the tables of the periodic system. In the Harkins table clusters of three elements are placed at each point of intersection of the inner helix with what would normally be the inner zero column. Similar arrangements are made in other forms of the periodic table.

Since the elements of this unusual group are not zero valent, as are the inactive gases occupying the corresponding column of the outer series, no reason exists for calling the group the zero sub-group. It is usually called the eighth. In the inner series, the maximum positive valence rises in steps of one from the copper group [1] to manganese. From this regularity the prediction might be made that in the eighth group the valence eight positive should be shown. In ruthenium and osmium tetroxides, RuO_4 and OsO_4, as well as in osmium octafluoride, OsF_8, this expectation is realized. But the other elements are not octavalent.[2]

The elements iron, cobalt, and nickel are abundant, the others of the group are relatively rare. The first three are fairly active, but the others are chemically so inactive that they, together with gold, are called the "noble metals," for they are not corroded by air or readily attacked by acids. The group is, therefore, usually divided into two sections known as the iron group and the platinum group respectively.

The Iron Group

Iron is found in large deposits of various ores. The most important of these are haematite, Fe_2O_3, magnetite, Fe_3O_4, and siderite, $FeCO_3$. Hydrated forms, or mixtures with clay

[1] The copper group is the only one which is irregular in that copper and gold have a valence greater than one in some of their compounds.

[2] The formula of one of the iron carbonyls is $Fe(CO)_4$, and that of nickel carbonyl, $Ni(CO)_4$. This is taken by some writers to indicate that iron and nickel are octavalent. Carbon monoxide seems to be contained as such in the compounds; that is, the compounds belong to the coordinative type, and the CO is a molecular group rather than a radical of valence two. Hence it is difficult to say what the valence of the metals in these compounds should be called.

such as iron-stone are common. Pyrite, FeS_2, is also an abundant mineral; but it is used chiefly to obtain sulfur dioxide for sulfuric acid manufacture, because the extraction of pure iron is more difficult from the sulfide ore than from the others. Iron is a constituent of haemoglobin, and is consequently of the utmost importance to life.

The abundance of the element, the ease with which it is extracted from its ores, and the manifold uses to which it may be put have made it one of the most important factors in modern civilization. So great has been the influence of its utilization on the progress of mankind that various stages in the development of human society are often called the stone, the bronze and the iron ages. The iron age might again be subdivided; the development of steel manufacture in the last century or two has made possible the industrial era in which we now live.

Review of the Manufacture of Iron and Steel

The ores are usually roasted to convert all compounds of iron into oxides. The function of the **blast furnace** is the reduction of the oxides to free metal. A mixture of coke, limestone, and the ore is introduced into the furnace, and a blast of preheated air passed through the heated mixture. The coke burns to carbon monoxide, which is the reducing agent, and the heat of the reaction melts the iron formed. The liquid metal, together with the slag which floats on it, is collected in a crucible at the bottom of the furnace. The slag is skimmed from the top, and the iron tapped off at the bottom. If the metal is not to be further treated it is cast into "pigs" in steel moulds. The temperature conditions and amounts of materials must be carefully regulated, because the yields obtained are determined by a complex equilibrium made up of the following reversible reactions:

$$C + CO_2 \rightleftarrows 2CO$$

$$Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2$$

$$FeO + CO \rightleftarrows Fe + CO_2$$

Cast Iron.—The pig iron obtained from the blast furnace contains from 92–94 per cent of iron, 2.6–4.3 per cent of carbon, silicon, manganese, and a little phosphorus and sulfur. This impure iron has physical properties quite different from those of the pure metal. It melts without first softening appreciably at a temperature several hundred degrees below the melting point of pure iron. It is brittle and very hard. Because it expands somewhat on cooling, it is largely used in making castings, and is for this reason also called **cast iron.** If the melted material is cooled rapidly, as when poured into metal molds, the carbon separates out in the form of the compound Fe_3C (cementite). The mixture is called chilled cast iron. If the melt is cooled slowly, the exothermic decomposition of the carbide has time to proceed, and the carbon is present in part as graphite. The product is gray cast iron, which is softer than the first variety. White cast iron is intermediate between the other two varieties.

Wrought Iron.—The brittleness and hardness of cast iron make it unfit for many uses. Since these properties are due to the impurities in the metal, iron intended for purposes requiring strength and toughness rather than hardness, is purified by reheating the metal on a bed of iron oxide in a reverberatory furnace. During the process of burning out the impurities by oxygen of the air, the melting point of the material rises toward that of pure iron, and the liquid becomes less and less fluid. The mixture is stirred or "puddled" to keep it all in contact with air. Finally it becomes so stiff that it can be formed into large balls weighing from 100 to 150 pounds each. While still hot, these are rolled out to remove mechanically retained impurities. The **wrought iron** thus obtained is relatively pure (99.8–99.9 per cent) and is very tough.[1] It is used for making wire, chains, bolts, etc., but for many purposes low carbon steel is replacing wrought iron.

Steel.—Cast iron, because of its high carbon content, is very hard and brittle; wrought iron, which is almost free from carbon,

[1] The toughness of wrought iron is thought to be due in part to films of slag not completely pressed out by the rolling. The slag imparts a fibrous structure to the iron.

is relatively soft. By regulating the amount of carbon, the properties of iron can, therefore, be adapted to a wide variety of uses. The name **steel** is given to mixtures of carbon and iron, almost free from phosphorus, sulfur, and silicon, and intermediate in carbon content between wrought and cast iron. Steel is hard and elastic, and has great tensile strength. Although variation in the amount of carbon alone makes possible the manufacture of steels possessing these properties in varying degrees, the adaptability of steel is further increased by the addition of other metals, such as chromium, nickel, tungsten and so on. Most of the important alloys of this kind have been mentioned in earlier portions of the text.

The Manufacture of Steel.—In the manufacture of steel, the two most important objects to be accomplished are the removal of impurities such as carbon, sulfur, phosphorus and silicon, and the introduction of carbon and the alloying metals in the proportions required to produce steel of the desired properties. The purification is effected by passing a strong current of air through or over the melted iron. Silicon is converted to silicon dioxide, which unites with oxides of manganese, and of iron to form silicates; these separate as slags and are easily removed. Carbon is oxidized to carbon monoxide, which burns at the mouth of the vessel. Oxidation of phosphorus and sulfur leads to the formation of oxides which would again be reduced to the free elements by metallic iron. For this reason converters used to make steel from ores rich in these two elements are lined with " basic " substances (such as magnesium oxide) which unite with the acidic oxides of phosphorus or sulfur. When the reactions are complete, carbon and any metal to be used are added, usually in the form of pure cast iron, spiegeleisen, or other iron alloys.

The Bessemer Process.—Two types of devices are used for carrying out the operations described above. The older of the two is the Bessemer process. Molten pig iron is poured into the converter (Fig. 30), shaped somewhat like a crucible, except that the opening at the top is relatively narrow. The blast of air is introduced through openings in the bottom. Just as in the manufacture of wrought iron, removal of impurities is

accompanied by a rise of the melting point, but in the Bessemer process the mix remains molten because the heat of the reactions maintains a sufficiently high temperature. Melting of the steel jacket of the converter is prevented by the use of linings of clay and sand, or (in special cases, as pointed out in the preceding paragraph) of basic oxides. After completion of the reactions and addition of carbon and the alloying metals, the converter is tilted to pour out, first the slag, and then the heavier molten metal.

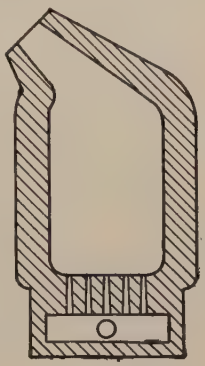


FIG. 30.

The Open-Hearth Process.—The reactions occurring in the Bessemer converter proceed with great speed. Although this is desirable for the production of large quantities of steel in a short time, accurate regulation of the process is difficult under these conditions. In the **Siemens-Martin Open-Hearth,** process (Fig. 31) the reactions go on more slowly, and permit both

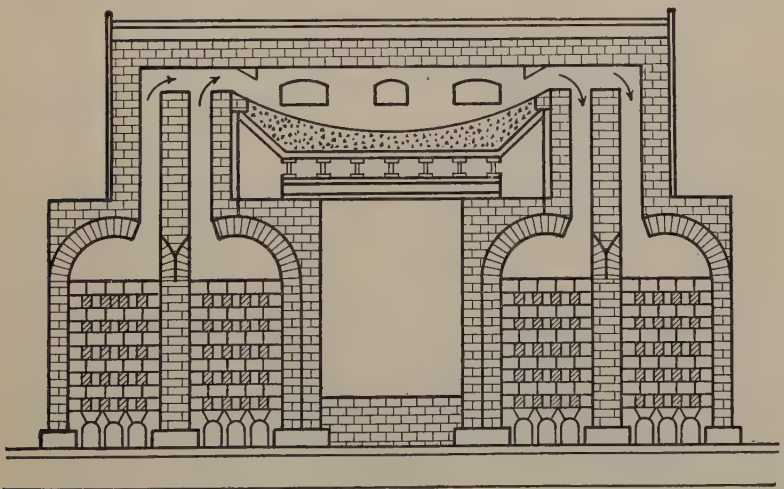


FIG. 31.

Taken from *Smith's College Chemistry* through the courtesy of the editor, Prof. J. Kendall, and the Century Company.

accurate temperature control and chemical analyses of the material from time to time. The cast iron is melted in a hearth, which resembles an enormous saucer covered with a roof made of silicon brick. The materials are heated from eight to ten hours with gaseous fuel. The high temperature required is secured not only by the reverberatory type of furnace used, but also by preheating the air, which passes over the melt to oxidize impurities. The gases are heated by passing them through a "checker-work" of brick which is kept hot by the escape of the spent gases through another portion of the device. In this process the cast iron, which is rich in carbon, is mixed with scraps of iron plate to lower the carbon content, and an oxide ore is added in proper proportions to aid in the oxidation of phosphorus, sulfur and silicon. The reactions are stopped when the desired amount of carbon is present and the impurities have been burned away. The material is drawn off into ladles in which mixtures with other metals are made when desired; often aluminium is added in small amounts to remove dissolved oxygen. In recent years an alloy of iron and titanium, which removes both oxygen and nitrogen, has been extensively used in place of aluminium to prevent the formation of gas bubbles in the ingots.

Special steels are sometimes prepared in crucibles made of graphite and fire clay, or in electric furnaces. These steels are used especially for making tools, springs, and so on.

Tempering.—Molten iron is capable of dissolving carbon. Part of the latter is present as the free element, part of it reacts with the iron to form the carbide, cementite, Fe_3C. With lowering of temperature, the solubility of carbon in the iron decreases. If cooling is very rapid, a supersaturated solid solution of carbon results and the steel thus obtained is hard and brittle. If cooling is slow, the cementite gradually separates in very small crystals. Below about 700° almost complete separation of the solution into pure iron and iron carbide occurs. Such steel is thus a mechanical mixture of soft iron and hard cementite. The hardness and toughness of steel may, therefore, be altered by reheating, and by regulating the temperature and the rate, as well as the duration of cooling. This process is called tempering.

Cobalt and Nickel.—Cobalt and nickel are found combined with arsenic, as in smaltite, $CoAs_2$, or with sulfur as in cobaltite, CoAsS and pentlandite (Ni, Cu, Fe)S, or with silica as in garnierite, which is a silicate of nickel and magnesium. Cobalt is not manufactured in large amounts, since only few uses for it have been discovered. The alloy, **stellite** (cobalt, chromium, tungsten) is used for high-speed tools, because it keeps its temper even better than special steel alloys; it is also used for surgical instruments and penknives because it does not rust. Nickel ores are usually "bessemerized." Certain ores containing both nickel and copper yield an approximately one to one alloy of the two metals, known as Monel metal. This is used in sheet metal work because it is not readily corroded by air or by acids. Nickel may be purified by electrolysis or by the Mond process. In the latter, the powdered impure metal is treated with cold carbon monoxide for the preparation of gaseous nickel carbonyl, $Ni(CO)_4$, from which pure nickel is later deposited by heat. Nickel is used in making alloys, such as special steels, German silver (copper, zinc, nickel), and coinage metal (copper, nickel). It is also used extensively to plate other metals. Nickel is not readily attacked by alkalies at high temperatures, and nickel crucibles are therefore useful for carrying out alkaline fusions. Finely divided nickel is an important catalytic agent in reactions of organic chemistry.

Magnetic Properties of the Elements of the Group.—When the north pole of one bar magnet is brought close to the south pole of another, the two magnets attract each other with a force depending on the strength of the two magnets. But the attractive force is also affected by the nature of the substance between the two magnets. It is customary to consider the force exerted when the two are in a vacuum as the basis of comparison. Paramagnetic substances diminish this attraction, diamagnetic substances increase it. All elements belong to the one or the other class. But in iron, nickel, and cobalt the magnetic properties are much more pronounced than in the other elements; they were at one time believed to be the only ones which affected or were affected by magnets. These elements are paramagnetic, but much more strongly than any others. A special name,

ferromagnetism, is used to describe their magnetic behavior. Iron is far more strongly paramagnetic than cobalt or nickel, and cobalt somewhat more than nickel. Lewis has recently attempted to relate these magnetic properties to atomic structure, but the developments of this work have not as yet been sufficiently definite to warrant a discussion of his ideas here.

Chemical Properties of the Metals.—Iron is a moderately active metal, but its reactivity is greatly affected by impurities. Thus the purest iron does not react with cold water, although ordinary iron rusts readily in moist air or in water. The rate of rusting is also greatly increased by impurities in the water, especially carbon dioxide. Ordinary rust consists mainly of hydrated ferric oxide, $3Fe_2O_3 \cdot H_2O$, which is porous and brittle, and therefore does not protect the metal from further action of air and water. But when iron is heated in steam, the magnetic oxide of iron, Fe_3O_4, is formed, and this oxide does produce an adhering protective film on the metal. "Russia" iron is made in this way; ferric oxide, which may be formed in small amounts during the process, is reduced by heating the coated object in a current of producer gas (carbon monoxide and nitrogen). Iron acts readily with dilute acids, displacing hydrogen; it reduces nitric acid to nitric oxide or even to ammonium nitrate, depending on the concentration and temperature of the acid. It acts vigorously with the halogens and sulfur, and burns in oxygen.

Finely divided iron is considerably more reactive than massive iron. A particularly active form (pyrophoric iron) is conveniently prepared by thermal decomposition of ferrous oxalate in a current of hydrogen at about 435° C. This iron powder catches fire spontaneously in air, decomposes water rapidly at 50° to 60° C., and reacts very vigorously with all oxidizing agents.

Nickel and cobalt are somewhat less active than iron. They act more slowly with dilute acids and are not rapidly rusted in moist air. The state of division affects their reactivity also.

Simple Ferrous and Ferric Salts.—The **ferrous salts,** in which the valence of iron is two positive, are readily oxidized by air and other oxidizing agents to ferric salts, in which the iron has the

valence three positive. In the preparation of ferrous salts by action of dilute acids on iron, this oxidation is prevented by carrying the reaction out in a vessel with a relatively small opening so that the hydrogen evolved displaces the air. To obtain ferrous salts of high purity, the resulting solution must be evaporated in the absence of oxygen, as in a stream of hydrogen or in a vacuum. The halides, nitrate and sulfate are soluble in water; most of the other common inorganic salts and the hydroxide are but slightly soluble. **Ferrous hydroxide** is only a moderately strong base, and its salts are therefore somewhat hydrolyzed. Most of the anhydrous salts, such as the chloride (prepared by the action of gaseous hydrogen chloride on hot iron) are white;[1] the hydrated salts pale blue or pale green. The tendency to form hydrates and double salts is fairly great; both tendencies are illustrated in **ferrous ammonium sulfate,** $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, which is the most commonly used ferrous salt because it is least readily oxidized by air in the dry condition. The ammonium sulfate seems to replace one water molecule of the simple hydrated salt, $FeSO_4 \cdot 7H_2O$. Since ferrous salts are so readily oxidized they are excellent **reducing agents.** Their reactions with oxidizing agents such as nitric acid and the halogens have already been discussed (pages 307 and 218).

Ferric salts may be obtained by oxidation of ferrous compounds, by the direct action of oxidizing agents, such as chlorine, on metallic iron, or from ferric compounds (for example ferric oxide, Fe_2O_3) occurring in nature. When ferrous salts are oxidized in aqueous solutions by air, basic ferric salts are formed:

$$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4$$

The solubility relations of the ferric salts are similar to those of the ferrous salts although, in general, the latter are somewhat more soluble. **Ferric hydroxide** is a very weak base, and its salts are therefore decidedly hydrolyzed in aqueous solutions. Nevertheless, black **ferric sulfide,** Fe_2S_3, unlike the sulfides of aluminium and chromium (see pages 535 and 571), is precipitated by addition of ammonium sulfide to solutions of ferric salts; ammonium car-

[1] Note however that ferrous sulfide, FeS, and ferrous oxide, FeO, are black.

bonate produces a precipitate of **basic ferric carbonate,** which is slowly hydrolyzed to the hydroxide in the presence of water. Ferric salts are more highly colored than ferrous salts. Anhydrous ferric chloride, for example, is very dark green, almost black, and appears red in transmitted light. But ferric ion in solution is almost colorless; the yellow color observed in ferric salt solution is due largely to partial hydrolysis to reddish brown ferric hydroxide. **Ferric oxide** is red. It is used in the making of rouge.

Ferric hydroxide, though a very weak base, possesses practically no acid properties. Only when fused with some basic oxides does it form compounds such as franklinite, $Zn(FeO_2)_2$, which are an indication of the very slight acidity of the hydroxide. The **magnetic oxide** of iron, Fe_3O_4, is possibly a compound of ferrous and ferric oxides as indicated by the formula $Fe(FeO_2)_2$.

Ferric salts are **reduced** to ferrous compounds without difficulty. Metallic iron is for many purposes the most convenient reducing agent:

$$2FeCl_3 + Fe \rightarrow 3FeCl_2$$

Hydrogen sulfide, in acidified solutions of ferric salts, does not precipitate ferric sulfide, which is soluble in acids, but reduces the ferric to ferrous ion (see page 173). Obviously ferric salts must act as moderately good oxidizing agents.

The oxidation of ferrous and the reduction of ferric salts is further evidence for the reversibility of reactions of oxidation and reduction. The equilibrium involved is:

$$Fe^{++} \rightleftarrows Fe^{+++} + \epsilon$$

Consequently the addition of any substance having a great tendency to take up electrons drives the reaction to the right, whereas the addition of a reagent which readily loses electrons causes the reverse reaction. Thus chlorine converts ferrous to ferric salts, but iodine, which does not take up electrons so readily as chlorine, cannot oxidize ferrous compounds. On the other hand iodide ion, which loses electrons more easily than chloride ion, reduces ferric salts:

$$2FeCl_3 + 2KI \rightarrow 2FeCl_2 + 2KCl + I_2$$

The fact that ferric chloride exists in aqueous solution shows that chloride ions do not behave similarly.

Complex Compounds of Iron.—Although neither ferrous nor ferric ions form stable complex ions with ammonia, both show a marked tendency to form such ions with other substances. The most common compounds of this type are the complex cyanides and thiocyanates. When ferrous or ferric salts are treated with potassium cyanide, precipitates of the simple iron cyanides are presumably first produced, but these react with an excess of potassium cyanide to form the complex salts:

$$Fe(CN)_2 + 4KCN \rightarrow \underset{\text{potassium ferrocyanide}}{K_4[Fe(CN)_6]}$$

and

$$Fe(CN)_3 + 3KCN \rightarrow \underset{\text{potassium ferricyanide}}{K_3[Fe(CN)_6]}$$

The ferrocyanide is prepared commercially by heating iron filings and potassium carbonate with nitrogenous animal refuse, such as blood. The reaction product contains potassium cyanide and ferrous sulfide. These interact, when the mass is leached with warm water, to form the ferrocyanide according to the reactions given above. Potassium ferricyanide is prepared by treating the ferrocyanide with chlorine:

$$2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN_6)] + 2KCl$$

Ferrocyanides are yellow, ferricyanides, reddish brown.

The most interesting reactions of these substances occur with simple ferric and ferrous salts. When potassium ferrocyanide is treated with ferric chloride an intensely blue precipitate of Prussian blue (ferric ferrocyanide) is obtained:

$$4FeCl_3 + 3K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

The substance is used as a pigment in making paints and in laundry blueing. It is to be noted that the iron in the complex ion is bivalent, whereas the simple iron ion is trivalent. When, on the other hand, ferricyanides react with ferrous salts, a deep blue precipitate is also formed. The two blue substances are probably not identical although there has been considerable dispute about

the question. The second may be ferrous ferricyanide (Turnbull's blue) formed according to the equation:

$$3FeCl_2 + 2K_3[Fe(CN)_6] \rightarrow Fe_3[Fe(CN)_6]_2 + 6KCl$$

In this compound the iron in the complex is trivalent, and the simple iron ion is bivalent.[1]

Another interesting complex ion of iron is formed when ferric solutions are treated with thiocyanates (for example KCNS). The deep red color which results was once thought to be due to molecules of the substance $Fe(CNS)_3$. But this assumption is not tenable because the color persists even in extremely dilute solutions (containing as little as 1/10,000 per cent of ferric ion), although ferric thiocyanate is a salt and therefore highly ionized into colorless thiocyanate ion and almost colorless ferric ion. The deep red color is due to the formation of the complex ion $[Fe(CNS)_6]^{\equiv}$.

$$FeCl_3 + 6KCNS \rightarrow K_3[Fe(CNS)_6] + 3KCl$$ [2]

This reaction, like the one of ferric salts with ferrocyanides, is used as a sensitive test for ferric ion. The sensitiveness of the thiocyanate test may be increased by shaking the aqueous mixture of thiocyanate and ferric salt with ether, which extracts the red substance, and thus concentrates it.[3]

Blue Prints.—Ferric oxalate is stable when kept in the dark, but decomposes spontaneously into the corresponding ferrous salt under the influence of light:

$$Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2$$

Paper which has been dipped into a solution of the ferric salt and then dried, is therefore light sensitive. When such sensitized

[1] A large number of different compounds are formed when ferrous and ferric salts act on potassium ferri- and potassium ferrocyanides, respectively. Their exact nature is still uncertain. Only the simplest interpretation of the reactions is here presented. A more detailed discussion is found in "A Text-Book of Inorganic Chemistry." J. N. Friend. Volume IX, Part 2, pp. 225–227.

[2] The compound $Fe(CNS)_3 \cdot 9KCNS$ is also known, and is believed by some writers to be responsible for the color.

[3] The substance extracted by ether is probably $Fe[Fe(CNS)_6]$.

paper is covered with transparent paper or cloth on which a drawing has been made, and is then exposed to light, those portions which lie under the lines of the drawing are not affected. If the sheet is next dipped into a solution of potassium ferricyanide, only the background turns blue, and the reproduction of the original drawing remains white. In commercial blue print paper, ferric ammonium citrate is used instead of the oxalate, and the ferricyanide is applied in the manufacture of the paper. Consequently only exposure to light and washing are necessary.

Cobalt Compounds.—Unlike iron, cobalt forms but few simple salts in which it is trivalent. The bivalent salts are often deep blue in the anhydrous condition and pink when hydrated. Cobaltous hydroxide is only a moderately strong base, somewhat like ferrous hydroxide, and the cobaltous salts are therefore slightly hydrolyzed. In aqueous solution, cobaltous salts cannot be oxidized to cobaltic compounds, unless there is present some substance which combines with the cobaltic ion produced to form a stable complex ion. Cobaltous hydroxide, however, is oxidized by strong oxidizing agents such as bromine to cobaltic hydroxide $Co(OH)_3$. Cautious ignition of cobaltous nitrate yields cobaltic oxide, Co_2O_3, but at high temperatures the commercial oxide, cobaltous-cobaltic oxide, Co_3O_4, is obtained.

Whereas the simple cobaltous salts are stable and the simple cobaltic salts are not, the reverse is true of many complex salts. An extremely large number of complex trivalent cobalt salts exist. These are in practically all respects analogous to the complex salts of trivalent chromium (see page 572). Only three illustrations of complex cobaltic compounds will be given. When cobaltous chloride is treated with an excess of ammonia, a complex salt of cobaltous ion and ammonia is first formed. This substance is so unstable that it decomposes completely when the solution is evaporated. But if a current of air is passed through the solution for several days, the color changes to a deep purple. After oxidation by air is complete, concentrated hydrochloric acid precipitates the purple compound $[Co(NH_3)_5Cl]Cl_2$, which is called chloropentammine cobalt chloride. Another compound may be obtained by changing the conditions but slightly. Addition of a large excess of ammonium chloride to the mixture before air is

passed through it, causes the formation of brownish yellow hexammine cobaltic chloride, $Co(NH_3)_6Cl_3$, in addition to some of the pentammine. Another type of complex cobalt salt is obtained by the action of nitrous acid (prepared by mixing potassium nitrite with a little acetic acid) on cobaltous salts. This treatment results in the formation of the very slightly soluble potassium cobaltinitrite $K_3Co(NO_2)_6$, in which the trivalent cobalt is part of the negative ion. In the reaction, nitrous acid acts as the oxidizing agent, and nitrite ion removes the cobaltic ion as soon as formed by entering into a very stable complex ion with it.

Cobalt compounds are used as pigments in the manufacture of the deep blue cobalt glass and in making paints for the decoration of china and porcelain.

Nickel Compounds.—The behavior of nickel in its compounds is very similar to that of cobalt and of iron, except that even complex nickelic salts are unknown. The only compounds of trivalent nickel are the oxide and hydroxide, Ni_2O_3 and $Ni(OH)_3$ respectively. Nickelous salts are in general green. Bivalent nickel ion enters into a number of unstable complex ions, such as the blue $Ni(NH_3)_4^{++}$ and the lavender $Ni(NH_3)_6^{++}$ ions; nickelous salts also combine readily with water to form hydrates. The formation of the curious nickel carbonyl has already been mentioned. In all other respects the behavior of nickelous and the corresponding cobaltous compounds is very similar.

The Platinum Group Metals

The metals of the platinum group are very rare. They are usually found alloyed with each other in small particles, but occasionally occur in small amounts in gold ores. The chief deposits are in Russia (Ural mountains); smaller quantities are found in Colombia, California and some of the larger islands of the Pacific. Their uses depend upon their resistance to corrosion. Platinum, the most abundant, is used in jewelry, for crucibles and other scientific apparatus, and in electrical instruments (for contact points, electrodes, etc.). Its coefficient of expansion is not greatly different from that of glass; consequently platinum wires can be sealed into the latter, a property which is

used in many ways. The hardness of platinum is greatly increased by alloying it with relatively small amounts of iridium. Alloys of iridium and osmium are used in fountain pen points.

In spite of these varied uses of the platinum group elements, they are not discussed in detail because of the complexity of their compounds and because their high cost renders impossible laboratory experiments merely for the purpose of general instruction. The following description is therefore merely a very brief summary of their outstanding properties.

The elements all possess a silvery luster; they are quite dense and have high melting points. At ordinary temperatures they are resistant to almost all reagents, for even fluorine attacks most of them but slightly unless they are heated. Palladium is the only one of the group which is attacked readily by nitric acid. They are, however, acted on by alkaline oxidizing mixtures at higher temperatures. Thus platinum crucibles must not be used for fusing alkalies, and molten alkalies containing nitrates, or especially sodium peroxide, dissolve the metals quite readily. In agreement with the general lack of activity of the metals is the instability of their compounds. The halides, even the fluorides, are decomposed at moderately high temperatures into the free elements; the oxides and sulfides decompose even more readily.

In all of these respects, the elements differ markedly from the relatively active metals, iron, nickel and cobalt. But there are further differences related to those already brought out. Since the platinum group metals are evidently much less electropositive than the iron group metals, it is not surprising to find that the hydroxides of the former are not only very weak bases, but that they actually have acid properties. As a consequence, the halides of the platinum group metals are much more extensively hydrolyzed than the iron group halides, and simple sulfates, nitrates, etc., of the former are not definitely known.

All of the platinum group metals show a marked tendency toward formation of complex ions. All but ruthenium and osmium are known to form complexes with ammonia similar to those of cobalt or of chromium. All of them are found in complex ions with chloride, cyanide, sulfide, hydroxide, and

other negative ions. Of these, the ion, $PtCl_6^{=}$, has already been mentioned in connection with the action of *aqua regia* on platinum (page 321). But the platinum group elements have so great a tendency to revert to the elementary condition that reducing agents precipitate them even from these complex ions.

Another striking difference from the iron group is the valence of the platinum group metals. In the former the characteristic valence is two; the valence three is common in all types of iron compounds, and in complex salts of cobalt. In the platinum group the characteristic valence is four, although all of them also exhibit other valences as will be pointed out below.

In spite of the great differences between the two sections of the eighth group there is nevertheless a certain parallelism such as might be expected from their position in the periodic system. Thus osmium and ruthenium constitute a fairly closely related pair. They alone form volatile tetroxides in which their valence number is eight; osmium combines with fluorine to give an hexa- and an octa-fluoride, and the existence of similar compounds of ruthenium is suspected. Although they form many complex ions which resemble those of iron, they, like iron, do not form complexes with ammonia.

Rhodium and iridium constitute the second pair. They are least readily attacked by *aqua regia*, they are much harder than the rest, and are distinguished from the others by the stability of the complex compounds in which they are trivalent. In this respect they are like cobalt, as also in their great tendency to unite with ammonia and similar molecules in complex ions. Palladium and platinum, on the other hand, are the only ones which form chlorides in which they are univalent. They are seldom trivalent, but bivalent and tetravalent in many of their compounds.

EXERCISES

(1) Explain why the eighth group is not divided into three groups, headed respectively by iron, cobalt, and nickel.

(2) (*a*) Show by the valence relations of the iron group elements that the order in which they are placed in periodic tables is better than the order of their atomic weights. (*b*) Give further advantages of the

arrangement used by consideration of the relations between the iron and the platinum groups.

(3) Upon what factors does the hardness of steel depend? Only those mentioned in the text need be considered.

(4) What is the function of the processes carried out in the Bessemer converter?

(5) What are the advantages of the Open-Hearth process?

(6) What is the function of aluminium often added to the steel before it is allowed to harden? What are the advantages of titanium?

(7) Give as many reasons as you can for the statement that iron is a fairly active metal.

(8) Explain why ferrous salts are less hydrolyzed than ferric salts.

(9) What is the experimental evidence that oxidation of ferrous to ferric ion is a reversible process? Explain why ferric chloride is so much more stable than ferric iodide. (The latter spontaneously decomposes into the corresponding ferrous salt.)

(10) Why is a deep red color produced when ammonium thiocyanate is added to ferric salts?

(11) What are the chemical changes in blue print paper when it is exposed and developed?

(12) Contrast the properties of iron and cobalt compounds on the one hand, and cobalt and nickel compounds on the other.

(13) Name all the differences you can between the iron and the platinum divisions of the eighth group.

(14) Point out the similarities between the related pairs of elements in the platinum group.

REFERENCES

So much has been written on iron and steel that any selection among the many good books and articles must necessarily be somewhat arbitrary. A few typical ones are listed:

A, B, C of Steel—Edited by A. O. Backert. A non-technical book profusely illustrated, which deals with every phase of the steel industry. A collaboration by several men active in the steel industry. Purely descriptive.

Spring—Non-technical Chats on Iron and Steel. It is written in popular style, comprehensive and clear.

Rogers—Industrial Chemistry (1921). Chapter XVII, The Metallurgy of Iron and Steel.

Detailed books for specialists are not included.

For the platinum group metals, Chapter XLII, in Lowry, Inorganic Chemistry, is especially recommended.

ALPHABETICAL LIST OF BOOKS REFERRED TO IN THE TEXT

Except in the case of a few books which are referred to very often, the chapters of the text in which the reference is cited are indicated by Roman numerals. The small number of references to journals are not included in this list.

Alembic Club Reprints (Edinburgh). W. F. Clay (1893).

Number 2. Foundations of the Atomic Theory: comprising Papers and Extracts by John Dalton, William Hyde Wollaston, and Thomas Thomson (1802–1808), IV.

Number 3. Cavendish, Henry. Experiments on Air, VII.

Number 4. Foundations of the Molecular Theory: comprising Papers and Extracts by John Dalton, Joseph-Louis Gay-Lussac, and Amadeo Avogadro (1808), II.

Number 6. Davy, Sir Humphry. The Decomposition of the Fixed Alkalies and Alkaline Earths (1807–1808), XXXII.

Numbers 7, 8. The Discovery of Oxygen. Vol. 1, Experiments by Joseph Priestley (1775); Vol. 2, Experiments by Carl Wilhelm Scheele (1777), VII.

Number 9. Davy, Sir Humphry. The Elementary Nature of Chlorine (1809–1818), IX.

Number 12. Faraday, Michael. The Liquefaction of Gases. (Papers 1823–1845.) With an Appendix Consisting of Papers by Thomas Northmore on the Compression of Gases (1805–1806), III.

Number 13. The Early History of Chlorine. Papers by Carl Wilhelm Scheele (1774), C. L. Berthollet (1785), Guyton de Morveau (1787), J. L. Gay-Lussac and J. Thenard (1809), XI.

Alexander, Jerome. Colloid Chemistry. 2nd Ed. D. Van Nostrand Co., New York (1924), XXIX.

Bancroft, Wilder Dwight. Applied Colloid Chemistry. Theory. McGraw-Hill Book Co., New York (1921), XXIX.

Backert, A. O. (Editor). The A. B. C. of Iron and Steel. 4th Ed. Penton Publishing Co., Cleveland, O. (1921), XLI.

Bogue, R. H. Colloidal Behavior. 2 vols. McGraw-Hill Book Co., New York (1921), XXIX.

Bragg, W. H. and W. L. X-Rays and Crystal Structure. G. Bell and Sons, London (1915), XXIII.

Cartledge, G. H. Inorganic Physical Chemistry. Ginn and Co., Boston, (1924), V, VII, XII, XIII.

Desch, C. H. Metallography. Longmans, Green and Co., London, New York (1910), XXXI.

Findlay, A. The Phase Rule and Its Applications. 5th Ed. Longmans, Green and Co., London, New York (1923), IX.

Friend, J. A. N. A Text Book of Inorganic Chemistry. C. Griffin and Co., London (1914).

Garrett, A. E. The Periodic Law. K. Paul, Trench, Trübner and Co., London (1909), XXII.

Gregory, R. A. Discovery, or the Spirit and Service of Science. Macmillan and Co., London (1916), I.

Hildebrand, J. H. Principles of Chemistry. The Macmillan Co. (1918), XII, XIV, XV, XVIII, XXIX.

Holmes, H. N. General Chemistry. The Macmillan Co., 1921, XXIX.

Jeffries, Z., and Archer, R. S. The Science of Metals. McGraw-Hill Book Co., New York (1924), XXXI.

Kempton, P. H. S. Industrial Nitrogen. Sir I. Pitman and Sons, London, New York (1922), XX, XXI.

Knox, J. The Fixation of Atmospheric Nitrogen. 2nd Ed. D. Van Nostrand Co., New York (1921), XX, XXI.

Lewis, G. N. Valence and the Structure of Atoms and Molecules. Chemical Catalogue Co., New York (1923), XXIV.

Loring, F. H. Atomic Theories. Methuen and Co., London (1923), XXIV.

Lowry, T. M. Inorganic Chemistry. Macmillan and Co., London (1922).

Lowry, T. M. Historical Introduction to Chemistry. Macmillan and Co., London (1915), IV, VII, XI.

McCoy, H. N., and Terry, E. M. Introduction to General Chemistry, 2nd Ed. McGraw-Hill Book Co., New York, London (1920), XXVIII.

Martin, G. Chlorine and Chlorine Products. C. Lockwood and Son, London (1915), XI, XXV, XXXII.

Martin, G., and Foucar, J. L. Sulphuric Acid and Sulphur Products. C. Lockwood and Son, London (1916), XVI, XVII.

Martin, G., Smith, S., and Milson, F. The Salt and Alkali Industry. C. Lockwood and Son, London (1916), XXXII.

Maxted, E. B. Ammonia and the Nitrids. J. and A. Churchill. London (1921), XIX.

Mellor, J. W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Longmans, Green and Co., London, New York (1922).

Mellor, J. W. Modern Inorganic Chemistry. Longmans, Green and Co., London, New York (1918), VI.

Millard, E. B. Physical Chemistry for Colleges. McGraw-Hill Book Co., New York (1921), I, V, XII, XIII.

Mills, J. Within the Atom. D. Van Nostrand Co., New York (1921), XXIV.

Moissan. The Electric Furnace. (Transl. by Victor Lenher.) The Chemical Publishing Co., Easton, Pa. (1904), XXVIII.

Moore, F. J. A History of Chemistry. McGraw-Hill Book Co., New York (1918), IV, XIII.

Perrin, J. B. Atoms. (Transl. by D. H. Hammick.) Constable and Co., London (1920), II, V.

Pring, J. N. The Electric Furnace. Longmans, Green and Co. London, New York (1921), XX, XXI, XXVII, XXVIII, XXXVI.

Ramsay. The Gases of the Atmosphere. 4th Ed. Macmillan and Co., London (1915), XIX.

Rogers, A. Manual of Industrial Chemistry. 3rd Ed. D. Van Nostrand Co., New York (1921).

Ruer, R. The Elements of Metallography. (Transl. by C. H. Mathewson.) J. Wiley and Sons, New York (1909), XXXI.

Russell, A. S. An Introduction to the Chemistry of Radioactive Substances. J. Murray, London (1922), XXIII.

Russell, Bertrand. The A. B. C. of Atoms. E. P. Dutton and Co., New York (1923), XXIV.

Schwartz, R. The Chemistry of the Inorganic Complex Compounds. (Transl. by L. W. Bass.) John Wiley and Sons, New York (1923), XXXIV, XXXIX.

Slosson, E. E. Creative Chemistry. The Century Co (1921), XXVIII.

Smith's College Chemistry. (Revised by Kendall.) The Century Co., New York (1923), XXVIII.

Soddy, F. The Interpretation of Radium. 4th Ed. G. P. Putnam's Sons. New York (1920), XXIII.

Spring, L. W. Non-Technical Chats on Iron and Steel. Frederick A. Stokes Co., New York (1917), XLI.

Stewart, A. W. Recent Advances in Physical and Inorganic Chemistry. 4th Ed. Longmans, Green and Co., London, New York (1920), XXXVI, XXXVII.

Stewart, A. W. Some Physico-Chemical Themes. Longmans, Green and Co., London, New York (1922), XXII.

Stieglitz, J. The Elements of Qualitative Analysis. 2 vols. The Century Co., New York (1919), XV, XVIII, XXXII.

Thomson, J. J. The Electron in Chemistry. The Franklin Institute, Philadelphia (1923), XXIV.

Vickers, C. Metals and Their Alloys. H. C. Baird and Co., New York (1923), XXXI.

Washburn, E. W. Introduction to the Principles of Physical Chemistry. 2nd Ed. McGraw-Hill Book Co. New York, (1921), V.

Wysor, H. Metallurgy. 2nd Ed. The Chemical Publishing Co., Easton, Pa. (1914), XXXI, XXXIV, XXXV, XXXVII, XXXIX.

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The Roman numeral following many of the titles refers to the chapter in which the subject is systematically treated, the Arabic numeral following the Roman refers to the page of the chapter on which the discussion begins. The symbol (e) after the name of an element means that under it are listed the properties of the element only; in such a case the name of the element is later repeated followed by the symbol (c). Under this heading the compounds are listed. In some cases, one or more of a series of page references is printed in heavy type to indicate those in which the systematic treatment of the subject is given. The symbol * indicates a table or a curve.

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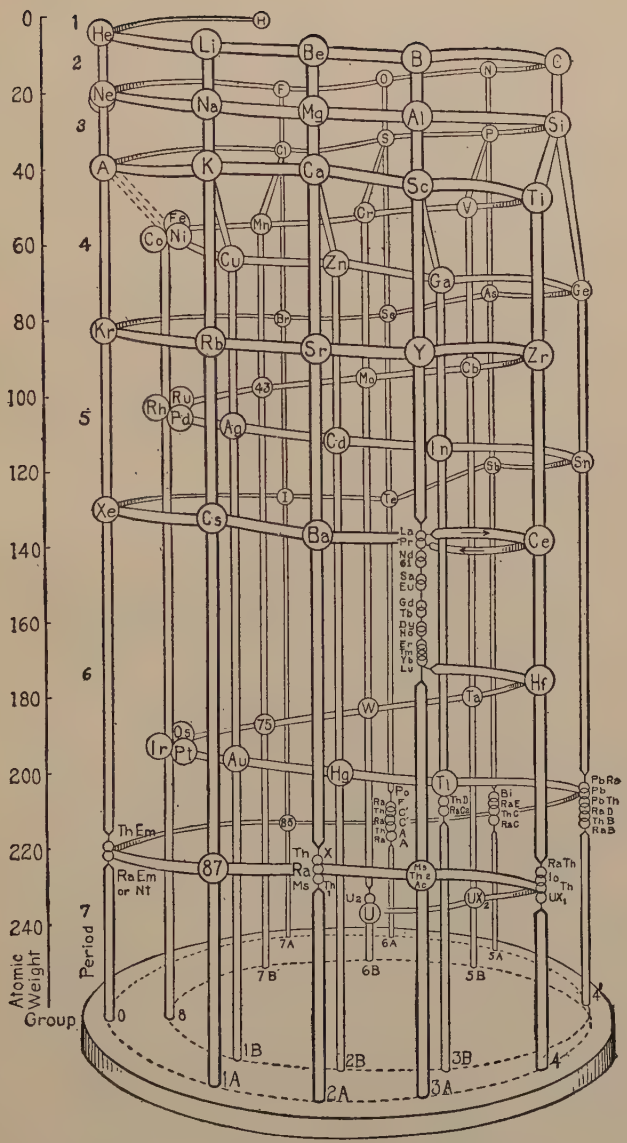

Periodic Table by W. D. Harkins

(See page 333, Schlesinger's General Chemistry.)

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INTERNATIONAL ATOMIC WEIGHTS, 1925

Name	Symbols	Atomic Weights	Atomic Numbers	Name	Symbols	Atomic Weights	Atomic Numbers
Aluminium	Al	26.97	13	Magnesium	Mg	24.32	12
Antimony	Sb	121.77	51	Manganese	Mn	54.93	25
Argon	A	39.91	18	Mercury	Hg	200.61	80
Arsenic	As	74.96	33	Molybdenum	Mo	96.0	42
Barium	Ba	137.37	56	Neodymium	Nd	144.27	60
Bismuth	Bi	209.00	83	Neon	Ne	20.2	10
Boron	B	10.82	5	Nickel	Ni	58.69	28
Bromine	Br	79.916	35	Nitrogen	N	14.008	7
Cadmium	Cd	112.41	48	Osmium	Os	190.8	76
Caesium	Cs	132.81	55	Oxygen	O	16.000	8
Calcium	Ca	40.07	20	Palladium	Pd	106.7	46
Carbon	C	12.000	6	Phosphorus	P	31.027	15
Cerium	Ce	140.25	58	Platinum	Pt	195.23	78
Chlorine	Cl	35.457	17	Potassium	K	39.096	19
Chromium	Cr	52.01	24	Praseodymium	Pr	140.92	59
Cobalt	Co	58.94	27	Radium	Ra	225.95	88
Columbium	Cb	93.1	41	Radon (Niton)	Rn	222.0	86
Niobium	Nb			Rhodium	Rh	102.91	45
Copper	Cu	63.57	29	Rubidium	Rb	85.44	37
Dysprosium	Dy	162.52	66	Ruthenium	Ru	101.7	44
Erbium	Er	167.7	68	Samarium	Sa	150.43	62
Europium	Eu	152.0	63	Scandium	Sc	45.10	21
Fluorine	F	19.00	9	Selenium	Se	79.2	34
Gadolinium	Gd	157.26	64	Silicon	Si	28.06	14
Gallium	Ga	69.72	31	Silver	Ag	107.880	47
Germanium	Ge	72.60	32	Sodium	Na	22.997	11
Glucinum	Gl	9.02	4	Strontium	Sr	87.63	38
Beryllium	Be			Sulfur	S	32.064	16
Gold	Au	197.2	79	Tantalum	Ta	181.5	73
Helium	He	4.00	2	Tellurium	Te	127.5	52
Holmium	Ho	163.4	67	Terbium	Tb	159.2	65
Hydrogen	H	1.008	1	Thallium	Tl	204.39	81
Indium	In	114.8	49	Thorium	Th	232.15	90
Iodine	I	126.932	53	Thulium	Tu	169.4	69
Iridium	Ir	193.1	77	Tin	Sn	118.70	50
Iron	Fe	55.84	26	Titanium	Ti	48.1	22
Krypton	Kr	82.9	36	Tungsten	W	184.0	74
Lanthanum	La	138.91	57	Uranium	U	238.17	92
Lead (ordinary)		207.20	82	Vanadium	V	50.96	23
Lead (Uranium)	Pb	206.06	82	Xenon	Xe	130.2	54
Lithium	Li	6.939	3	Ytterbium	Yb	173.6	70
Luticium	Lu	175.0	71	Yttrium	Y	88.9	39
				Zinc	Zn	65.38	30
				Zirconium	Zr	91.0	40